BULLETIN 555 OCTOBER, 1935

Some Physiological Studies with Calcium Cyanamide and Certain of Its Decomposition Products

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FOREWORD

This publication is one of a series dealing with orchard fertilizers. Viewpoint and practice have changed considerably during the past few years, both as to materials used for fruit tree fertilization and the time of application. This has called for new sets of experiments in which the problems are studied from the standpoint of the chemical changes of the fertilizers in the soil, the general tree response, soil reaction changes, depth of penetration of the amendments in relation to soil types and the absorbing root area, temperature of the soil, and other closely correlated factors.

Cyanamid has come into rather general use in Ohio and the results to date indicate that as satisfactory results are secured with it as from any other carrier of nitrogen. This has been true with all the tree fruits.

In the present paper the studies deal more particularly with the physiological aspects of plants treated with this carrier of nitrogen; however, due to continued interest and use of Cyanamid by orchardists, the more practical aspects have been continued and a later publication will deal more particularly with the orchard results secured.

Fall applications of Cyanamid are giving as great a growth and yield of both apples and peaches as spring treatments. Growers find it more convenient to apply it at that time because of a better distribution of labor. The autumn treatments may begin about the middle of September and extend at least to the middle of November. Early spring treatments of Cyanamid may be made during the latter part of February or during March but late spring treatments should be avoided, particularly on very light soils.

The application should be at the approximate rate of a quarter of a pound for each year of the tree's age until 5 pounds have been applied to a peach tree and 8 or 10 pounds to an apple tree.

J. H. Gourley

SOME PHYSIOLOGICAL STUDIES WITH CALCIUM CYANAMIDE AND CERTAIN OF ITS DECOMPOSITION PRODUCTS

R. M. SMOCK

INTRODUCTION[1]

Cyanamid is a nitrogen fertilizing material whose main constituent is calcium cyanamide. Cyanamid is a grayish black material. It is sold in both a granular and pulverized form.

Numerous investigations have been carried out to determine the chemistry of the decomposition of calcium cyanamide in the soil and the gross crop responses to this fertilizing material. Little or no attention has been directed to the physiological phases of the plants' responses, however. Workers have offered only speculations as to which decomposition product or products were utilized by the plants. One of the specific purposes of this investigation was to furnish evidence as to which compound or compounds are directly absorbed and serve as sources of nitrogen for protein synthesis.

There are only scant references in the literature to the specific effects of the decomposition products of calcium cyanamide on plants when they are supplied individually. Difficulties in the use of calcium cyanamide on very sandy soils have been speculatively attributed to a number of decomposition products which might accumulate in the soil in sufficient quantity to cause plant injury. No definite attempt has been made heretofore to determine which compound or compounds may be responsible for such difficulties. In an effort to throw light on these problems, the various decomposition products of calcium cyanamide have been supplied individually in nutrient solutions to determine their gross effects on the peach, apple, and tomato.

It has been shown that hydrogen cyanamide, one of the primary decomposition products of calcium cyanamide, may be effectively hydrolyzed to urea by certain colloidal and mineral materials. No attempt has been made to grow plants with calcium cyanamide as a source of nitrogen in a medium composed of mixtures of some of these materials with pure sand. However, there are reported herein experiments showing the utilization of the nitrogen from calcium cyanamide by the tomato when it is grown in pure sand to which have been added small amounts of certain effective catalysts.

Moreover, a limited number of agronomic studies has been carried out by other workers to determine the influence of soil reaction values on the utilization of the nitrogen from calcium cyanamide by plants. An attempt is made in this investigation to determine at what soil reaction value the nitrogen from this material is most efficiently utilized by peach and apple seedlings.

CHEMISTRY OF CALCIUM CYANAMIDE

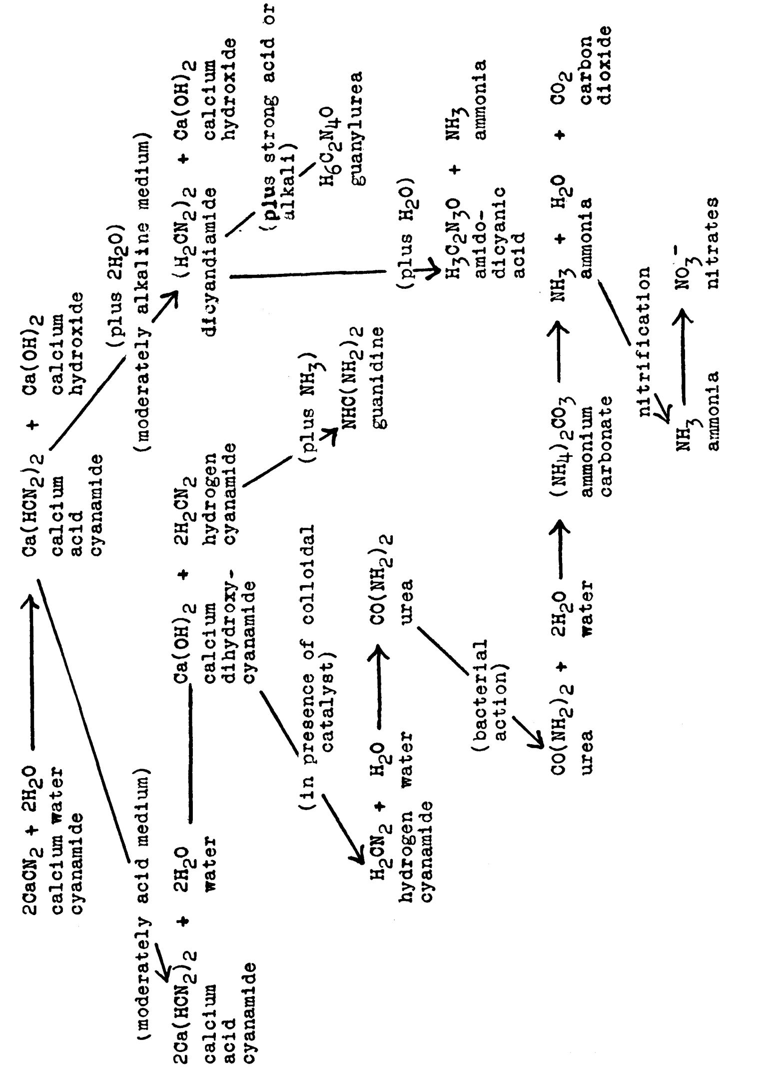
LITERATURE DISCUSSION

To avoid confusion in this literature discussion on the chemistry of calcium cyanamide, the commercial product will be spoken of as "Cyanamid" and the pure salt as "calcium cyanamide".

[1]Acknowledgment—The author wishes to express his appreciation to Drs. J. H. Gourley and F. S. Howlett for their invaluable aid in planning various phases of this investigation.
Manuscript received for publication August 1934.

As it is manufactured in this country, Cyanamid contains approximately 63.0 per cent calcium cyanamide, 17.0 per cent calcium hydroxide, and 12.0 per cent free carbon. Small amounts of calcium sulfide, calcium carbonate, silica, iron, and alumina are also present. The total nitrogen content of Cyanamid is approximately 22 per cent. Small amounts of oil are added to condition the pulverized type of Cyanamid and a special granulating agent (calcium nitrate) is used with the granular material. The calcium cyanamide in Cyanamid is 98 per cent soluble in water.

DECOMPOSITION OF CALCIUM CYANAMIDE



Summarized accounts of the chemistry of calcium cyanamide are supplied by Pranke (37), McCool (30), Williams (52), and Buchanan and Barsky (8). A summarized compilation of their accounts appears in the diagram on Page 4, which depicts the major reactions involved in the decomposition of calcium cyanamide.

Hydrogen cyanamide (also called "free cyanamide" and "acid cyanamide") is the nitrile of carbamic acid and has been assigned two possible structures by Conant (9), $NH{=}C{=}NH$ and $NH_2{-}C{\equiv}N$. Both of these forms may be present in solution. It behaves as a weak mono-basic acid with a dissociation constant of 5.4×10^{-11} at 25° C., according to Crowther and Richardson (13). It precipitates an insoluble silver salt from alkaline silver nitrate, the precipitate being insoluble in ammonia.

Calcium cyanamide is the calcium salt of hydrogen cyanamide. As indicated in the diagram it may be hydrolyzed to form either hydrogen cyanamide or dicyandiamide.

Dicyandiamide is a very stable compound and is not readily soluble in water. It is formed by the polymerization of hydrogen cyanamide in the pH range of 8.0 to 12.0, according to Buchanan and Barsky (8).

LITERATURE REVIEW

DECOMPOSITION IN THE SOIL

To comprehend fully the plants' responses to Cyanamid, one should have some knowledge of the chemistry of the decomposition of calcium cyanamide in the soil. The monograph of Pranke (37) gave a rather complete compilation of the work done with calcium cyanamide up to 1913. Williams (52) has given a rather full discussion of its chemistry. McCool (30) has reviewed over 300 references on the properties and uses of calcium cyanamide.

Just what the agencies of the decomposition of calcium cyanamide in the soil are is a moot question. All the investigators seem to agree that the decomposition as far as hydrogen cyanamide is entirely chemical in nature, but there is disagreement as to whether the change from thence to urea is physico-chemical or biological in nature.

PHYSICO-CHEMICAL THEORY OF THE HYDROGEN CYANAMIDE TO UREA CHANGE

Kappen (23), Ulpiana (49), and Stutzer *et al.* (46) were among the first to assert that the change was physico-chemical in nature. Kappen (23) concluded that iron, manganese, and aluminum compounds have some relation to this hydrolysis of hydrogen cyanamide to urea. Crowther and Richardson (13) found that decomposition was accomplished by a number of mineral constituents of the soil. They found that the zeolites, prehnite and apophylite, were particularly effective catalyzers. Pranke (37) and Cowie (12) both asserted that the change was due to certain soil zeolites. Kubiena (25) attributed the hydrolysis to certain electrolytes and "soil colloids". Rhodin (39) found that animal charcoal and certain by-products of iron bearing iron, manganese, and aluminum were effective catalyzers of the hydrogen cyanamide to urea change.

BIOLOGICAL THEORY OF THE HYDROGEN CYANAMIDE TO UREA CHANGE

Lohnis and Sabashnikoff (26) were among the few workers who asserted that the hydrolysis could be attributed to bacterial action.

The bulk of the evidence points to a physico-chemical explanation of the catalysis of the hydrolytic change.

FORMATION OF AMMONIA, NITRATES, GUANIDINE, DICYANDIAMIDE, AND GUANYLUREA IN THE SOIL

Following the formation of urea in the Cyanamid decomposition process, there is a rapid ammonification of the urea in non-sterile soils. After the formation of the ammonia, the usual nitrification process takes place with the production of nitrates.

The literature makes no mention of an appreciable formation of guanidine or guanylurea following Cyanamid applications to the soil. Both of these compounds are potential decomposition products in the soil and may form in very small amounts in certain instances. They are essentially laboratory products of artificial decomposition, however.

Dicyandiamide may be formed in alkaline solutions up to a pH of 12.0, according to Buchanan and Barsky (8). De Ruitjer (16) reported that the addition of alkaline salts to a soil caused a formation of dicyandiamide. Pranke (38) stated that exposure to air caused 80 per cent of the hydrogen cyanamide to be converted to dicyandiamide in a year's time. In good agricultural practice very little if any dicyandiamide is formed in the soil. Pranke (37) stated that as long as the dicyandiamide does not exceed 10 per cent of the total nitrogen present, it will do no harm to plants. Cowie (11) opposed the older ideas of Immendorf (21), who claimed that dicyandiamide is produced in poor soils and those of acid nature or those with low bacterial activity.

THE AVAILABILITY OF THE NITROGEN OF CALCIUM CYANAMIDE TO FRUIT CROPS

McCool (30) has given a rather complete report of the work done with agronomic crops in regard to the response to Cyanamid. He concluded that when it was properly used, Cyanamid was a satisfactory source of nitrogen for these crops. Since our investigation was concerned with certain horticultural crops, the literature citations will be limited to that subject.

Marsh (27, 28) applied Cyanamid 2 weeks before bloom to the apple and peach and found it inferior to the other common nitrogen sources. The soil on which the orchard was situated was not well adapted to tree growth.

Davis (15) found Cyanamid unavailable to apple trees when supplied in solution to sand cultures. Davis took no recognition of the necessity of colloidal material in the growing medium for hydrolysis of the hydrogen cyanamide formed from the calcium cyanamide. He also failed to take account of the hydrolytic products in his nutrient solution.

Harlan and Collison (19) reported that calcium cyanamide was a satisfactory nitrogen source for apple trees on the heavier types of soil. HofMann (20) obtained a marginal leaf burn when amounts over 5 pounds per tree were used with apple trees growing on a very shallow soil in a hillside orchard.

McCalla (29) indicated that Cyanamid was as good a nitrogen source for various fruit crops as nitrate of soda or sulfate of ammonia when applied in the very early spring or in the fall.

Cooper and Wiggin (10) found that this source of nitrogen was as satisfactory as the other common nitrogen carriers for the apple in Arkansas. Anderson (2) reported that Cyanamid was as efficient a source of nitrogen for the currant as other common nitrogen carriers.

METHODS OF PROCEDURE

SAND CULTURES

For the sand cultures 3-gallon glazed earthenware pots supplied with drainage openings were used. The sand employed was a mixture composed of two-thirds "diamond sandblast" and one-third "crystal silica". The sand mixtures were well washed with tap water and finally with distilled water.

The Shive and Stahl (45) method of constant renewal of solutions was employed. The 2-quart reservoirs were placed on adjustable benches so that the rate of flow was regulated by the height of the supporting bench. Two quarts of solution dripped from the reservoirs every 24 hours. Solutions were allowed to drip 6 days, and on the seventh day the pots were flushed with distilled water.

The nutrient solutions employed were modifications of those described by Tiedjens and Blake (48). Distilled water was used for all solutions. Stock solutions of the various chemicals were made with a concentration of one-half molar (with the exception of hydrogen cyanamide which was one molar). Final nutrient solutions were prepared in 5-gallon carboys.

PLANTS USED IN EXPERIMENTS

One-year-old Elberta peach trees and one-year-old apple seedlings of uniform size were used. In Experiment III both peach and apple trees had been grown from seed in the soil beds employed in the study.

Tomato plants of the Marhio variety were grown in flats and then transplanted into 3- or 4-inch pots containing a rich soil. After they had reached a height of 4 to 6 inches, uniform plants were selected for the various studies. Before the plants were transplanted into the soil or sand cultures, the soil was completely washed from the roots. In all cases, the tomato plants were kept deflorated during the course of the experiments to permit maximum vegetative growth.

CHEMICALS USED IN EXPERIMENTS

Chemically pure materials were used in the preparation of nutrient solutions with the exception of the calcium cyanamide used for hydrogen cyanamide preparations.

Calcium cyanamide was used in the commercial form. Fresh Cyanamid was obtained each season and immediately upon receipt was placed in sealed jars. With the exception of Experiment III the powdered form of Cyanamid was used to avoid the complications involved in the use of calcium nitrate as a granulating agent.

When the soil was treated with Cyanamid, it was applied as uniformly as possible by spreading it through a fine-meshed wire screen.

MACROCHEMICAL METHODS

Total nitrogen was determined by the Gunning (4) modification of the Kjeldahl method in order to include nitrates. The Scales and Harrison (41) method of boric acid distillation was employed. Twenty-five- to 50-gram samples of fresh material were dried for moisture determinations and the dry material was used for total nitrogen analyses. The most satisfactory method of drying the samples was one suggested by Nightingale (34), in which fresh material was spread evenly over a wire screen tray and then dried in a steam-heated oven at 60° C. A constant flow of air was supplied in the oven by an electric fan. The samples were finally dried to complete dryness in a vacuum oven at 80° C. The dried samples were ground in a Nixtamal mill, and one-gram samples were taken for total nitrogen determinations.

Soluble nitrogen was determined by the cold water extraction method described by Nightingale *et al.* (35) and also by the hot water extraction method described by Davidson and Shive (14). When samples could not be extracted immediately they were frozen and stored.

Nitrates were determined by the Sessions and Shive method (44) which involves aeration into 0.02 normal acid over a 12-hour period with Devarda's alloy after the ammonia has been removed.

Ammonium analyses were made by the aeration method described by Davidson and Shive (14).

For qualitative dicyandiamide determinations 15 to 50 grams of fresh material were ground in a Nixtamal mill and then macerated with coarse sand in a mortar when necessary. Extraction was made by shaking well with 300 milliliters of water for one-half hour. Four grams of "Darco" were added and shaken well with the mixture. The soluble extract was then filtered off and the Harger (18) method of determination was used.

For qualitative hydrogen cyanamide determinations, extraction was carried on as described for dicyandiamide analyses and then the method described by Buchanan (7) was employed.

MICROCHEMICAL METHODS

Freshly cut sections from washed plant material were used in the microchemical studies. Samples were taken at approximately the same time each day and approximately the same soil depth. At least three sections were used in each test.

Nitrates, ammonium, free-reducing substances, proteins, and starch were detected by methods described by Sampson (40). Nitrates were determined by the use of the Diphenylamine and Nitron reagents. Ammonium was detected by the use of Nessler's reagent and by the formation of ammonium-magnesium-phosphate crystals. Free-reducing substances were studied by heating the sections for one minute with Fluckiger's reagent on a boiling water bath. Starch was studied by the use of iodine - potassium iodide solution. Proteins were observed by the use of Millon's reagent and the xanthoproteic reaction.

Free and combined cyanide analyses were made by the use of sodium picrate paper with 30 grams of freshly ground material covered with 10 per cent sulfuric acid.

Urea was determined by the method described by Fosse (17). The test is based on the formation of dixanthylurea crystals. The sections were enclosed by a Van Tieghem cell covered by a cover slip. A drop of acetic acid was added to the section from a capillary pipette and a few grains of solid xanthyhydrol were added. Needle crystals of typical character formed in the presence of urea.

Attempts were made to modify the qualitative tests for dicyandiamide and hydrogen cyanamide for microchemical purposes but the tests were not sensitive enough for microchemical purposes. There is great need for the development of adequate microchemical tests for these compounds.

HYDROGEN-ION DETERMINATIONS

Unless otherwise indicated, potentiometric determinations of hydrogen-ion concentrations were made with the use of the quinhydrone electrode. In a few instances the La Motte-Morgan colorimetric test for pH was employed for soil samples.

PRESENTATION OF DATA

EXPERIMENT I

One of the purposes of this experiment was to determine the decomposition product or products of calcium cyanamide which are absorbed and utilized by the tomato and peach. The second main purpose of the experiment was to gain some knowledge of the general nitrogen metabolism of the tomato following treatments with Cyanamid. This second purpose was accomplished by studying the nitrogen fractions of Cyanamid-treated and untreated tomatoes in soil cultures.

It is apparent that it would be desirable to use sand cultures for a study of the intake and utilization of the nitrogen from calcium cyanamide. This procedure was impossible since certain amounts of colloidal material are required in the growing medium for satisfactory decomposition of calcium cyanamide. A variety of soils, ranging from a very sandy to an organic type of soil, was employed in this experiment.

Likewise, it would be advantageous in such a study to use large amounts of fertilizing material so that accumulations of the various decomposition products might be produced in such quantity that macrochemical measurements of the amounts might be made. Large applications of Cyanamid with pot cultures are impossible due to the danger of injury. Plants growing in pots are shallow rooted and more susceptible to fertilizer injury.

GENERAL PROCEDURE OF EXPERIMENT I

In this study of the intake and utilization of Cyanamid nitrogen, it seemed necessary to make daily measurements of the various products within the plant. Due to the small accumulations of the various compounds in the soil, microchemical determinations seemed much more desirable than macrochemical ones. However, in the second main phase of the experiment macrochemical determinations seemed more feasible.

Nine- and 10-inch unglazed clay pots supplied with drainage were used. Tap water was supplied to the plants as often as seemed desirable for optimum growth. The soils used were almost completely air dried and then screened. In the soils that were low in fertility, minus nitrogen nutrient solutions were periodically supplied to the plants.

The synthetic soils were mixed on a volume ratio basis. The sand employed in making the synthetic soils was a white silica sand described under "general methods". The clay subsoil used in these mixtures was taken from a Wooster silt loam profile.

EXPERIMENT I: SERIES 1

The purpose of this series was to determine the decomposition product or products of Cyanamid which were absorbed and utilized by the tomato and peach. Daily microchemical observations were made to observe the possible intake of urea, ammonium, and nitrates and to observe possible changes in the content of free-reducing substances, starch, and proteins inside the plants.

Both the fibrous roots and petioles of the tomato and the fibrous roots of the peach were examined daily. Samples were taken at approximately the same time each day. Root samples were taken at approximately the same depth, with no sample being taken below a depth of 4 inches.

The microchemical results are expressed on a relative basis: Zero indicates complete absence; one, a trace; two, a small amount; three, a moderate amount; four, a large amount; and five, a very abundant amount.

The plants were not treated with Cyanamid until there was a consistently low amount of ammonium and, if possible, only a small amount of nitrates within the plants. The first determination given in the data in each case is that obtained on the first day after treatment.

Tomato—½ *sand-½ subsoil.*—On April 17, 1933, 40 uniform Marhio plants were transplanted into a synthetic soil composed of one-half white silica sand and one-half subsoil. On May 15, 1933, 15 plants were treated at the rate of approximately 400 pounds to the acre (i. e., one gram per pot) and five plants were left untreated. The pH of the soil at the beginning of the study was 5.83 and at the conclusion, 6.80.

From day to day there were no significant changes in free-reducing substances, starch, or protein in either the petioles or roots, but at the end of the experiment there were differences between treated and untreated plants. The treated plants were lower in free-reducing substances and starch and higher in proteins than the untreated ones. Since the data indicated no significant daily changes, they are not included in the graphs.

The amounts of ammonium and nitrates observed in the untreated plants were consistently low throughout the whole period of the experiment. By the end of the period the plants were apparently free of nitrates and ammonium.

The results from the analyses for ammonium obtained with the treated plants appear in Figure 1. Following treatment with Cyanamid there was an increase of ammonium in the roots on the third day and in the petioles on the fourth day. This increase persisted irregularly in the petioles until the fifteenth day after treatment. There was a similar persistence in the roots until the twenty-fourth day. The benefit of the treatment was dissipated by the twenty-fourth day.

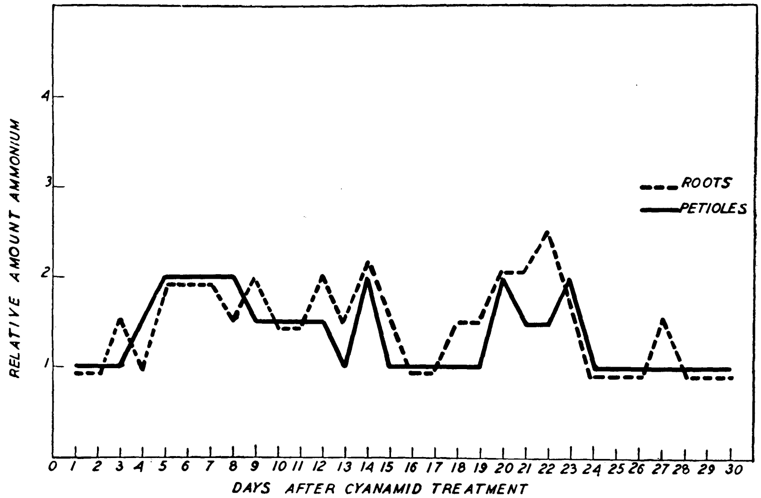


Fig. 1.—Relative amounts of ammonium nitrogen in roots and petioles from tomatoes growing in ½ sand-½ subsoil following Cyanamid treatment

On the fourth day following treatment there was an increase in the amount of nitrates in the petioles, but this increase soon fell off and the amount was consistently low thereafter. Nothing significant could be observed in the roots as to the amounts of nitrates. It will be noted in Figure 2 that the amounts of nitrates were very erratic from day to day. The watering process in its nitrate leaching action may have been responsible for this.

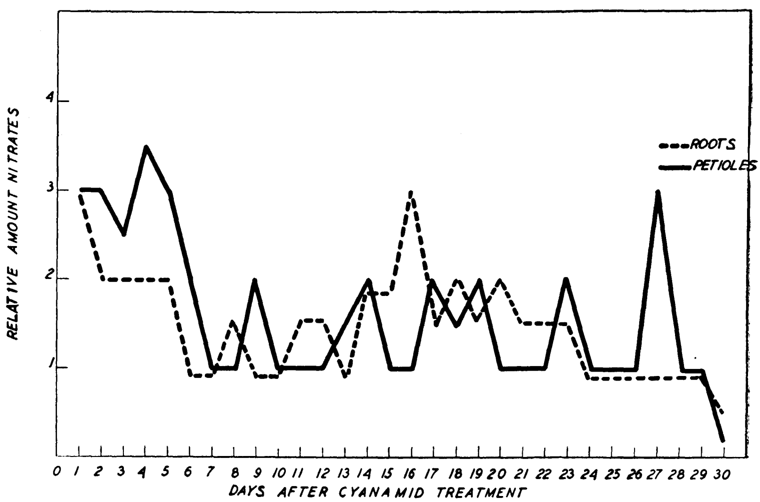


Fig. 2.—Relative amounts of nitrate nitrogen in roots and petioles from tomatoes growing in ½ sand-½ subsoil following Cyanamid treatment

Tomato—*coarse sand-compost.*—On June 7, 1933, 18 Marhio plants were transplanted into a synthetic soil composed of 6-year-old compost mixed with coarse bank sand. The compost had been used several times during the 6-year period and was thought to be poor in fertility. There were approximately three parts of compost to one of sand in the mixture. On June 22, 1933, treatments of the 18 plants were made with Cyanamid at the rate of 200 pounds to the acre (i. e., 0.5 gram per pot). The pH of the soil at the beginning of the study was 6.12 and at the end, 6.40.

The data relative to the amounts of ammonium appear in Figure 3. On the second day following the treatment, the ammonium content of the roots increased and this increase persisted until the twenty-first day. The ammonium increase in the petioles appeared on the third day and it persisted until the twenty-first day.

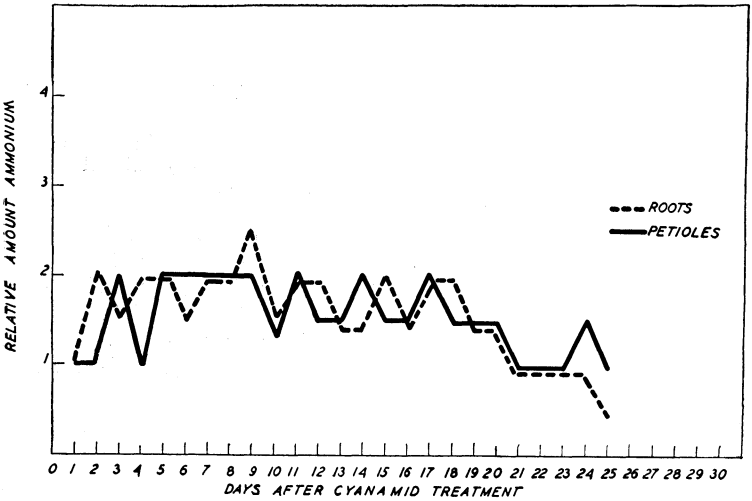


Fig. 3.—Relative amounts of ammonium nitrogen in roots and petioles from tomatoes growing in sand-compost mixture following Cyanamid treatment

There was an increase of nitrates in the roots on the third day after treatment, with a more or less irregular persistence of this increase until the twelfth day. In the petioles there was a nitrate increase on the second day, with the increase being apparent until the thirteenth day.

Urea could not be detected in the roots at any time. Tests for free-reducing substances, starch, and proteins were not made.

Tomato—¾ *sand*-¼ *subsoil.*—On June 8, 1933, 20 Marhio plants were transplanted into a synthetic soil composed of one-fourth subsoil and three-fourths white silica sand.

On June 22, 1933, fifteen plants were treated at the rate of 200 pounds of Cyanamid to the acre (i. e., 0.5 gram per pot). Five plants were left untreated. On June 25 a slight injury was noted on the foliage of the treated plants. It should be stated that the injury occurred on a very sandy type of soil. Within a week the plants had fully recovered from the injury and were growing satisfactorily.

The ammonium data appear in Figure 4. Observations indicated an ammonium increase in the roots of the treated plants on the fourth day after treatment. Such an increase was apparent in the petioles on the fifth day; this increase persisted until the seventeenth day. Very soon after this date the foliage began to become yellowed from lack of nitrogen.

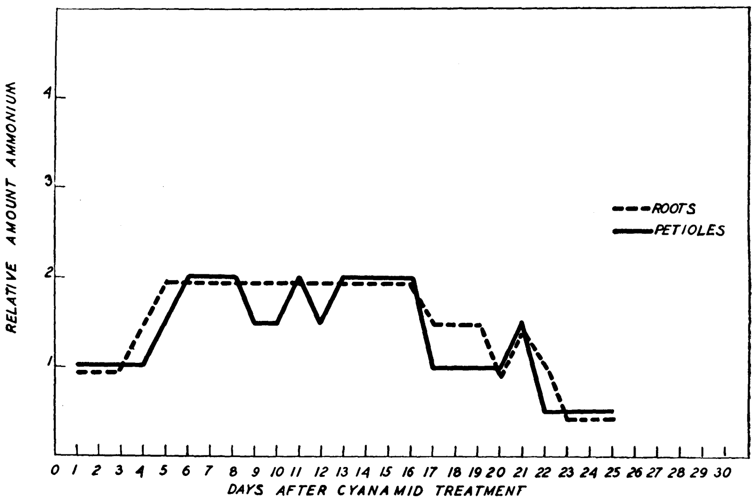


Fig. 4.—Relative amounts of ammonium nitrogen in roots and petioles from tomatoes growing in ¾ sand-¼ subsoil following Cyanamid treatment

The nitrate data were erratic and irregular and very hard to interpret on a quantitative basis. Nothing significant can be deduced from them.

For 3 days following the Cyanamid applications there was a positive test for urea in the roots of the treated plants. This was the only set of plants in the soil cultures which gave a positive test for urea. It is possible that in such a sandy soil a sufficient quantity of urea had accumulated to permit an entrance *per se* into the plant.

Peach—¾ *sand-¼ subsoil.*—On April 7, 1933, six one-year-old peach seedling trees were planted in a synthetic soil composed of three-quarters white silica sand and one-quarter subsoil. On May 9 three trees were treated at the rate of 200 pounds to the acre (0.5 gram per pot) of Cyanamid and three were left untreated. A second treatment was given on May 23 to the treated trees. The soil pH at the start of the test was 6.12 and at the end, 7.06.

After the first Cyanamid treatment there was an increase in the ammonium content of the roots on the second day. There was a rather irregular persistence of this increase. After the second treatment there was an increase on the second day. Again there was an irregular persistence until the seventeenth day.

Peach—½ *sand-½ subsoil.*—On April 7, 1933, six one-year-old peach seedlings were placed in a synthetic soil composed of one-half white silica sand and one-half subsoil. Treatment of three trees on May 9 and again on May 23 was made with Cyanamid at the rate of 200 pounds to the acre (i. e., 0.5 gram per pot). The soil pH at the start of the test was 5.83 and at the end, 7.34.

There was an increase in the roots of the treated plants on the second day after the first treatment and there was an irregular persistence of this increase until the twelfth day. There was an increase in nitrates on the third day and an irregular persistence of this increase thereafter until the twelfth day. After the second Cyanamid treatment there was an increase in nitrates on the first day.

In no instance was urea detected in the roots of these trees; this is in contrast to the tomato cited above.

EXPERIMENT I: SERIES 2

The purpose of this series was to examine macrochemically the nitrogen metabolism of Cyanamid-treated tomato plants growing in soil cultures. It was desired that quantitative observations might be made of certain nitrogen fractions in plants that were Cyanamid-treated and untreated. Such a study would offer confirmation of microchemical data obtained in Series 1 which indicated increases in ammonium and nitrates in plants following Cyanamid treatment.

Frequent applications of Cyanamid were made to insure sufficient accumulation of ammonium and nitrates in the soil to permit their macrochemical detection in tomato plants. The treatments were small to avoid possibilities of plant injury.

Two soil types were employed in this study in order to observe the effect of soil type on the nitrogen utilization of Cyanamid.

Tomato—*Wooster silt loam.*—This set of plants was grown in a Wooster silt loam having a reaction of 5.6 pH at the start of the test. Twenty-two plants were treated with Cyanamid at the rate of 400 pounds to the acre (i. e., 1.00 gram per pot) 2 days before the plants were transplanted into them. The material was mixed into the surface 2 inches of soil. Twenty-two pots were left untreated.

After the plants were well established in the pots, frequent but small applications of Cyanamid were made to the pots in the treated group. Individual applications were usually made at the rate of 50 pounds to the acre (i. e., 0.125 gram per pot). The total amount of Cyanamid added to each treated pot was at the rate of 850 pounds per acre.

After the plants had grown for 23 days in the soil cultures, they were harvested. Some of the plants were slightly larger than others in both the treated and untreated groups. The larger and smaller plants were grouped separately for nitrogen analyses.

The weights of the tops of Cyanamid-treated and untreated plants growing in Wooster silt loam appear in Tables 1 and 2. The Cyanamid-treated plants in both size groups were greater in weight than the untreated ones. The per cent of moisture in the treated plants was also greater than that in the untreated ones, indicating a greater succulence in the former.

The results of the analyses for various nitrogen fractions appear in Tables 1 and 2. The Cyanamid-treated plants in both size groups had more ammonium nitrogen in the stems than did the untreated plants. There was more nitrate nitrogen in the treated plants also. These data are taken to indicate that both ammonium and nitrates are absorbed *per se* by the tomato plant following Cyanamid treatments. Of course, there is often more ammonium nitrogen in nitrate-treated plants than in untreated plants and the data do not prove that the larger amount of ammonium in the Cyanamid-treated plants results solely from its entrance *per se* from the soil. However, the data from Series 1 indicate that there is an entrance of ammonium into Cyanamid-treated plants prior to that of nitrates.

TABLE 1.—Nitrogen Fractions in Whole Stems of Cyanamid-treated and Untreated Tomato Plants in Wooster Silt Loam*

(Large plants)

Treatment	Average weight of plants	Dry matter	Ammonium	Nitrates	Nitrate-ammonium free soluble nitrogen	Total soluble nitrogen
	Gm.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Cyanamid............	87.36	6.52	0.172	0.299	1.919	2.390
Untreated............	66.72	7.89	0.046	0.148	1.106	1.300

*The nitrogen fractions are expressed as per cent of dry matter.

TABLE 2.—Nitrogen Fractions in Whole Stems of Cyanamid-treated and Untreated Tomato Plants in Wooster Silt Loam*

(Small plants)

Treatment	Average weight of plants	Dry matter	Ammonium	Nitrates	Nitrate-ammonium free soluble nitrogen	Total soluble nitrogen
	Gm.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Cyanamid	65.90	7.83	0.107	0.284	1.559	1.950
Untreated............	41.27	9.88	0.014	0.004	1.352	1.370

*The nitrogen fractions are expressed as per cent of dry matter.

The data show that in both the treated and untreated plants there was more ammonium and nitrate nitrogen in the larger plants than in the smaller.

There was more total soluble and soluble nitrate – ammonium free nitrogen in the Cyanamid-treated plants than in the untreated ones. This indicates that the increased intake of nitrogen due to Cyanamid treatments resulted in increased synthesis of soluble organic nitrogen.

Tomato—½ ***sand-½ subsoil.***—This set of plants was grown in a synthetic soil composed of one-half white silica sand and one-half subsoil. The reaction of the mixture at the start of the test was pH 5.8. Two days prior to transplanting the plants into the pots 12 pots were treated with Cyanamid at the rate of 400 pounds to the acre (i. e., 1.00 gram per pot) and 12 were left untreated. The material was well mixed into the surface 2 inches of soil. Minus nitrogen nutrient solutions were applied to all of the pots periodically throughout the test.

After the plants were well established in the pots, frequent but small applications of Cyanamid were made to those pots which had been treated previously. Individual applications were usually made at the rate of 50 pounds to the acre (i. e., 0.125 gram per pot). The total amount applied to each treated pot was at the rate of 750 pounds to the acre.

After growing for 43 days the plants were harvested. The weights of the tops of both treated and untreated plants appear in Table 3. It is apparent from the weight data that the treated plants did not have a very large advantage over the untreated ones. There was a more striking difference in the appearance of the plants than the weight data would indicate. The untreated plants were much lighter green in color than the treated ones.

Duplicate samples of the whole stems were taken for analyses. The results appear in Table 3.

TABLE 3.—Nitrogen Fractions in Whole Stems of Cyanamid-treated and Untreated Tomato Plants in ½ Sand-½ Subsoil*

Treatment	Sample	Average weight of plants	Dry matter†	Ammonium	Nitrates	Nitrate-ammonium free soluble nitrogen	Total soluble nitrogen
		Gm.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Cyanamid.....	1	97.91	10.00	0.138	0	1.582	1.720
Cyanamid.....	2	....	10.00	0.110	0	1.610	1.720
Untreated.....	1	95.00	10.00	0.055	0	0.965	1.020
Untreated.....	2	....	10.00	0.048	0	0.632	0.680

*The nitrogen fractions are expressed as per cent of dry matter.
†Failure to obtain moisture determinations demanded that an arbitrary per cent of dry matter be assumed.

The data indicate that there was considerably more ammonium in the stems of the tomato plants that were treated with Cyanamid than in those that were untreated.

In neither the treated nor the untreated plants could any nitrates be detected. This fact does not preclude the possibility of the entrance of some nitrate nitrogen into the plants, for nitrates may not have accumulated in the soil sufficiently to make available to the plants any more than was utilized in protein synthesis.

The data also indicate a greater amount of total soluble and nitrate-ammonium free soluble nitrogen in the treated plants than in the untreated ones. There is undoubtedly a greater synthesis of soluble organic nitrogen compounds in Cyanamid-treated plants than in untreated ones.

DISCUSSION OF EXPERIMENT I

Other investigators have shown that following Cyanamid treatments there is an accumulation of ammonium in the soil. One of the explanations of such an accumulation is that there is a retarded nitrification, as indicated by Cowie (12) and Mujerkii (33). A second explanation offered by Bradfield (6) is that the ammonium from ammonium hydroxide forms a more stable ammonium complex in the soil than that from ammonium sulfate.

As a result of this persistence of ammonium in the soil following Cyanamid applications, the possibility of ammonium absorption by the plant is offered. Following Cyanamid treatments the ammonium content of the fibrous roots of both the peach and tomato showed an increase on the second to fifth day.

Variations in the date of the increase seemed to depend on the amount of colloidal or organic material in the growing medium. The greater the colloidal or organic content of the medium, the more quickly did the ammonium increase appear in the plants. This ammonium increase following treatments persisted from 15 to 25 days until it was reduced in the course of the normal protein synthesis process. There was also some indication that the greater the colloidal content of the soil the longer was this persistence.

Following the ammonium increase in the plants studied, there was an increased amount of nitrates apparent in the plants. In most cases the nitrate increases followed that of ammonium by one to 3 days. The persistence of the nitrate increase in plants after Cyanamid treatments was very erratic and difficult of interpretation.

Urea was detected in the roots of Cyanamid-treated plants in only one instance. The plants in which it was observed microchemically were growing in a synthetic soil composed of three-quarters silica sand and one-quarter subsoil. Under most circumstances, it is likely that the urea formed from Cyanamid decomposition in the soil is rapidly ammonified and there is little, if any, entrance of urea *per se* into the plants.

Daily differences in the amounts of free-reducing substances, starch, and proteins could not be discerned. Differences between treated and untreated plants were noted, however. Cyanamid-treated plants were more vigorous and the content of proteins was higher than in untreated plants. Starch and free-reducing substances were found in larger amounts in the untreated plants as a result of less protein synthesis.

Macrochemical data on the differences in certain nitrogen fractions of Cyanamid-treated and untreated tomato plants in two soil types were obtained. In both the synthetic sandy soil and the silt loam soil, there was considerably more ammonium in the treated plants. In the sand-subsoil mixture, no nitrates could be detected quantitatively in the plants, but, in the case of the plants growing in the silt loam, there was considerably more nitrate nitrogen in the treated plants. There was probably enough sand in the synthetic soil to permit considerable leaching of nitrates. Another possible explanation of the lack of nitrates in the plants in the sand-subsoil is that these plants were 20 days older and had received less total nitrogen than those in the silt loam.

In both the sand-subsoil mixture and the silt loam the plants that were Cyanamid-treated had a greater content of synthesized soluble nitrogen and more total soluble nitrogen than those that were untreated.

Judging from the weight data and the appearances of the plants, it may be said that the greater response to Cyanamid was made in the silt loam, but these plants had had 20 days more in which to make response.

EXPERIMENT II

The general purpose of this experiment was to determine the specific effects of the various decomposition products of Cyanamid on plants of the peach, apple, and tomato. Under certain field conditions (i. e., large applications and on very sandy soils), some difficulties have been experienced from the use of Cyanamid as a fertilizer. Marsh (27) and HofMann (20) have reported injury to the apple with Cyanamid treatments. Marsh conducted his test on a very poorly drained soil, and HofMann carried on his work in a hillside orchard on very shallow soil. Watson (51) has reported injury to the peach on very sandy Florida soils following large applications of Cyanamid. Only speculations have been offered as to what decomposition product or products were responsible for the injury noted under these unfavorable conditions. By determining the effects of these compounds when supplied individually in sand cultures at various concentrations, it was hoped that some light might be thrown upon this problem. Such a study should also reveal the availability of the nitrogen of these compounds to plants in sand cultures.

Incident to the experiment a number of colloidal materials were mixed with sand in an attempt to hydrolyze hydrogen cyanamide to urea so that plants could utilize the urea and ammonium from Cyanamid in modified sand cultures. Various investigators (13, 39) have examined the effectiveness of certain colloids in catalyzing the hydrogen cyanamide to urea change, but none has employed such an artificial medium for the growing of plants.

EXPERIMENT II: SERIES 1

Various concentrations of hydrogen cyanamide, dicyandiamide, guanylurea, guanidine, sodium nitrate, calcium nitrate, urea, and ammonium sulfate were employed in this study.

GENERAL PROCEDURE: SERIES 1

The concentrations of the various compounds used in the nutrient solutions appear in Table 4. The amounts of potassium acid phosphate, magnesium sulfate, calcium chloride, and iron sulfate employed in this study were those suggested by Tiedjens and Blake (48). The final nutrient solutions had an osmotic concentration of approximately three-quarters atmosphere.

The hydrogen cyanamide was prepared from powdered Cyanamid according to the method described by Buchanan and Barsky (8). Sufficient Cyanamid (124 grams) was taken to give a stock solution of one molar concentration. Nitrogen determinations on the stock solutions of hydrogen cyanamide indicated that extraction did not always dissolve out the theoretical and desired concentration of this compound. Hence, the final concentration values of hydrogen cyanamide in the nutrient solutions are subject to some error since the theoretical and not the actual values are given.

Iron was supplied at the rate of from one to 50 milliliters of 0.02 per cent ferrous sulfate per 17 liters of nutrient solution. Boron was added at the rate of 0.5 to 2 milliliters of one per cent boric acid per 17 liters of nutrient solution. Several drops of 0.0000178 PVM[2] manganese sulfate were added to each 17 liters of solution. Half normal potassium hydroxide was added as needed to the urea and sulfate of ammonia solutions in order to give the desired reaction values.

The hydrogen-ion concentrations of the various nutrient solutions before and after passing through the pots are given in Table 5. The data for this table were taken from pots in which tomatoes were growing and were obtained 3 to 4 weeks after the start of the treatments.

Unless it is otherwise indicated in the discussion, all treatments were made in duplicate or triplicate. Only one plant or tree was put in each pot.

All plants were given a minus nitrogen nutrient solution (see Solution XIV, Table 4) until initial signs of nitrogen deficiency were apparent. This required 27 days for the peaches, 40 for the apples, and from 7 to 14 for the tomatoes.

[2]PVM refers to partial volume molecular concentration.

TABLE 4.—Concentration of Nutrient Solutions

Solution number	Plants used	Potassium phosphate KH_2PO_4			Magnesium sulfate $MgSO_4.7H_2O$			Calcium chloride $CaCl_2.2H_2O$			Ammonium sulfate $(NH_4)_2SO_4$			Urea $CO(NH_2)_2$		
		PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL
I........	Peach Tomato	0.0063	862	0.862	0.0023	584	0.584	0.00292	429	0.429	0.0056	740	0.740	....	....	....
II........	Peach Tomato	.0063	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	0.0016	100	0.10
III.........	Tomato	.0063	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
IV.........	Tomato	.0063	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
V..........	Tomato	.0063	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
VI..... ...	Tomato	.0063	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
VII........	Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
VIII.....	Apple Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
IX.......	Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
X........	Apple Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XI.......	Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XII......	Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XIII.....	Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XIV.....	Peach Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XV......	Peach Apple Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XVI......	Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....
XVII......	Tomato	.0062	862	.862	.0023	584	.584	.00292	429	.429	....	....	....	....	....	....

TABLE 4.—Concentration of Nutrient Solutions—Continued

Solution number	Plants used	Calcium nitrate $Ca(NO_3)_2.4H_2O$			Hydrogen cyanamide H_2CN_2			Dicyandiamide $(H_2CN_2)_2$			Guanylurea $N_4H_6C_2(SO_4)$			Guanidine $NHC(NH_2)_2SO_4$			Sodium nitrate $NaNO_3$		
		PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL	PVM	ppm	GPL
I	Peach, Tomato	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
II	Peach, Tomato	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
III	Tomato	0.00584	1380	1.38	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
IV	Tomato	.00584	1380	1.38	0.0032	150	0.15	...	...	...	...	...	...	...	...	...	...	...	...
V	Tomato	...	...	...	.0012	50	.05	...	...	...	...	...	...	...	...	...	...	...	...
VI	Tomato	...	...	...	.0025	100	.10	...	...	...	...	...	...	...	...	...	...	...	...
VII	Tomato	...	...	...	.0032	150	.15	...	...	...	...	...	...	...	...	...	...	...	...
VIII	Apple, Peach, Tomato	...	...	...	.0050	200	.20	...	...	...	...	...	...	...	...	...	...	...	...
IX	Peach, Tomato	...	...	...	...	...	...	0.00029	25	0.024	...	...	...	...	...	...	...	...	...
X	Apple, Peach, Tomato	...	...	...	...	...	...	.00059	50	.049	...	...	...	...	...	...	...	...	...
XI	Peach, Tomato	...	...	...	...	...	...	.00118	100	.099	...	...	...	...	...	...	...	...	...
XII	Peach, Tomato	...	...	...	...	...	...	...	...	...	0.0005	100	0.099	...	...	...	...	...	...
XIII	Peach, Tomato	...	...	...	...	...	...	...	...	...	...	...	...	0.00064	100	0.10	...	...	...
XIV	Peach, Tomato	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
XV	Peach, Apple, Tomato	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.00986	798	0.798
XVI	Tomato	...	...	...	.0050	200	.20	...	...	...	...	...	...	...	...	...	.00986	798	.798
XVII	Tomato	...	...	...	...	...	...	.00059	50	.049	...	...	...	...	...	...	.00986	798	.798

PVM refers to partial volume molecular.
ppm refers to parts per million.
GPL refers to grams per liter.

TABLE 5.—pH of Nutrient Solutions Before and After Passing Through Pots

Solution number	Nitrogen source	pH before drip	pH after drip
I	Ammonium sulfate	6.60	6.05
II	Urea	6.50	5.47
III	Calcium nitrate	4.50	3.80
IV	III plus hydrogen cyanamide	4.44	4.90
V	50 ppm hydrogen cyanamide	4.20	5.05
VI	100 ppm hydrogen cyanamide	4.20	5.00
VII	150 ppm hydrogen cyanamide	4.26	4.65
VIII	200 ppm hydrogen cyanamide	4.10	4.75
IX	25 ppm dicyandiamide	5.00	4.10
X	50 ppm dicyandiamide	5.25	4.10
XI	100 ppm dicyandiamide	4.02	4.65
XII	Guanylurea	4.52	4.22
XIII	Guanidine	5.00	4.85
XIV	No nitrogen	4.65	4.70
XV	Sodium nitrate	4.85	5.98
XVI	XV plus hydrogen cyanamide	4.66	5.30
XVII	XV plus dicyandiamide	4.62	6.22

Hydrogen cyanamide—*peaches.*—A summarization of the literature would indicate that hydrogen cyanamide is the compound responsible for the death of seeds in the soil when large applications of Cyanamid are made. Milo (31) found that hydrogen cyanamide was rather injurious in small concentrations to sugar cane. Pranke (37) thought the effect of hydrogen cyanamide would be less drastic than that of dicyandiamide. Crowther and Richardson (13) found that hydrogen cyanamide was the compound responsible for the killing of seeds when large applications of calcium cyanamide were made. It would also seem that there is an unavailable nitrogen compound which Milo (31) found to be directly injurious to sugar cane. The following experiment was made to observe the effects of various concentrations of this compound on the peach.

One-year-old Elberta peach trees were uniformly pruned to a single stem about 2 feet above the bud union and placed in sand cultures. After symptoms of nitrogen deficiency were apparent, 200 ppm[3] of hydrogen cyanamide in the nutrient solution (VIII) were given to the trees daily.

On the second day after the start of the treatments the foliage appeared slightly wilted. On the fourth day the first signs of definite injury to the foliage appeared. On the fifth day the leaves had irregularly burned margins; deeply indented and irregular areas around the margins of the leaves were becoming quite brown and a few of the badly affected leaves were starting to fall. Also, injury to the roots was first apparent on the fifth day; the tips of the roots and the fine rootlets were brown and quite dead.

By the twelfth day all the foliage was quite wilted and slightly shriveled from the apparent water deficit. More of the new young roots were injured and the injury was slowly involving the entire roots, after having started at the tips.

The treatment was discontinued on the fourteenth day. Many of the leaves were wilted and quite dry. There had been no visible growth during the treatment period. Almost all of the roots were injured. A typical plasmolysis of the root tip was followed by death of the tip and then gradual involvement of the whole root became apparent. After the first few days of treatment, defoliation ceased and no more leaves dropped thereafter. Figure 5 shows the typical injury on leaf and roots from a peach tree receiving this treatment.

[3]ppm signifies parts per million.

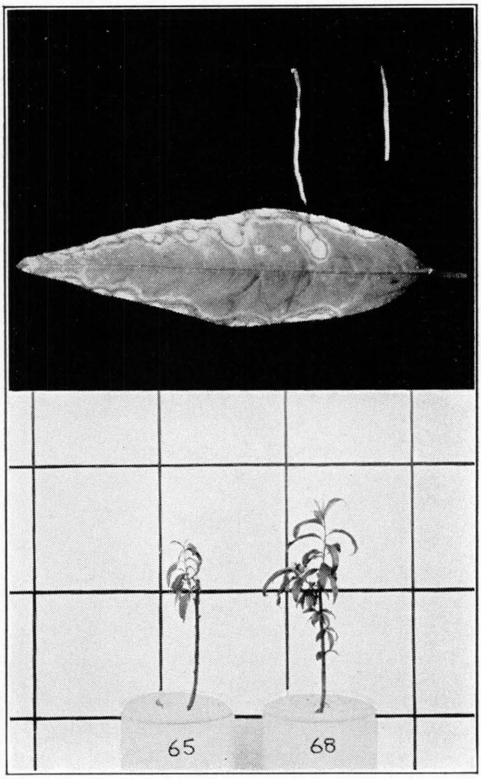


Fig. 5.—*Top*—Leaf and roots from peach tree receiving 200 ppm hydrogen cyanamide in the nutrient solution. (Samples taken 5 days after start of treatment).

***Bottom*—Tree 65. Elberta peach tree treated with 200 ppm hydrogen cyanamide in the nutrient solution. Tree 68. Elberta peach tree receiving sodium nitrate in the nutrient solution. (Picture taken on fourteenth day after start of treatment).**

A 7-gram sample of leaves from trees receiving this hydrogen cyanamide treatment was analyzed for hydrogen cyanamide on the day of the cessation of treatment. The test was negative.

Hydrogen cyanamide—*apples*.—The effects of a relatively high concentration of hydrogen cyanamide on the apple were examined in this study.

Uniform one-year-old apple seedlings were pruned to a single whip about 2 feet high and placed in the sand cultures. After initial signs of nitrogen deficiency were apparent, a treatment of 200 ppm hydrogen cyanamide in the nutrient solution (VIII) was started.

On the second day after the start of the treatment, the foliage appeared slightly wilted. Treatment was discontinued on the fourteenth day. Throughout the period of treatment the wilting became progressively worse and by the end of the period the leaves were dry and withered. There was no marginal burn on the leaves nor any other symptom of injury except the extreme wilting and drying up of the foliage. There was no growth during the period of treatment and the leaves were somewhat yellow from lack of nitrogen. The roots were injured in a manner very comparable to that described for the peach.

A 5-gram sample of the leaves was taken for a hydrogen cyanamide determination, but the test was negative.

Figure 6 (Bottom) shows a tree injured with this compound and also the extremely wilted and dessicated condition.

Hydrogen cyanamide—*tomato*.—Concentrations of 50, 100, 150, and 200 ppm of hydrogen cyanamide in nutrient solutions V, VI, VII, and VIII, respectively, were employed in this study.

On the fourth day after the initiation of the treatments the roots of the plants treated with 200 ppm hydrogen cyanamide had injured tips. Even though the weather was cool, the foliage showed a slight injury at this date. Small portions of the leaf margins were brown.

By the fifth day the plants treated with 200 ppm had a very definite injury to both roots and leaves. The injury was spreading back from the root tips and large portions of the roots were becoming involved. First indications of root injury appeared as plasmolysis of the outer portions and soon the root became brown and flaccid.

On the sixth day the plants treated with 150 and 100 ppm started to show a slight wilting and curling effect of the foliage. On the ninth day it was noted that the leaves on the plants receiving any concentration seemed more yellow than those receiving a minus nitrogen solution. On the tenth day it was apparent that there was a very slight amount of growth at the tops of the plants, even on the most seriously injured ones. It was determined microchemically that there was a small amount of urea in the hydrogen cyanamide stock solution. There may have been a very slight amount of hydrolysis to urea in the pure sand, also. At any rate it was assumed that the green portions at the tops of the plants were due to urea utilization and not to that of hydrogen cyanamide *per se*.

On the thirteenth day it was apparent that there was a serious injury to the stems of the plants beneath the surface of the sand at all concentrations above 50 ppm. Almost the entire cortex of the stem in this region was plasmolyzed and slowly became necrotic. On the fourteenth day a fading of the leaf margins to a whitish yellow was observed at concentrations above 50 ppm. There was also a slight curling of the edges of the leaves.

By the fifteenth day a small amount of growth could be seen on all plants treated with hydrogen cyanamide. The growth was of a rosette type. A cluster of small green leaves appeared at the top of the plant, and, after a few days, elongation of the stems occurred and the plant then was free of this rosette.

By the thirtieth day even the plants treated with 50 ppm were showing a slight leaf injury. There was a slight leaf tipburn, but the fading of the margins to a whitish yellow was more apparent.

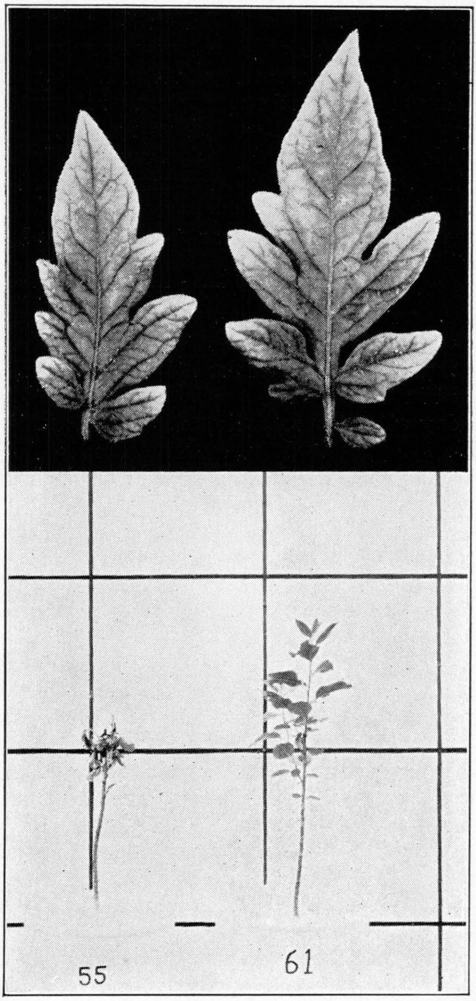


Fig. 6.—*Top*—Tomato leaves from plant receiving 150 ppm hydrogen cyanamide in the nutrient solution. (Picture taken on thirteenth day after start of treatment).

***Bottom*—Tree 55. 200 ppm hydrogen cyanamide in the nutrient solution.**
Tree 61. Sodium nitrate in the nutrient solution. (Picture taken on fourteenth day after start of treatment).

Throughout the period of the treatments it was observed that injury was accentuated by high temperatures in the greenhouse. Not only did the more severely injured plants wilt badly but the foliage injury seemed to be increased. Figure 6 (Top) shows hydrogen cyanamide injury to tomato leaves.

Samples of plants receiving the various treatments were taken for hydrogen cyanamide determinations. All tests were negative.

Hydrogen cyanamide plus calcium nitrate—*tomato*.—The purpose of this experiment was to observe the effect of a relatively high concentration of hydrogen cyanamide when an available source of nitrogen was added to the nutrient solution. Calcium nitrate in addition to 150 ppm hydrogen cyanamide (IV) was used in this treatment.

On the third day after the start of the treatment many of the leaves had a brownish black margin and a few small brown spots in them. The young tender shoots and leaves were badly curled. The tips of the roots were dehydrated and brown.

On the ninth day the plants had a very dark green foliage, but the injury had become progressively worse with more leaves and roots becoming involved. No growth was taking place even though there was a vigorous growth on the plants receiving calcium nitrate alone. The plants receiving this combination treatment wilted on warm days.

When treatments were discontinued on the thirty-seventh day, the plants had a very slight amount of growth of the rosette type described previously. The plants wilted badly on warm days. The roots were seriously injured (Fig. 7 Inset).

The harmful effect of this treatment appeared sooner and was more drastic than that with hydrogen cyanamide alone. Even though an available source of nitrogen had been added, the plants grew but very little. Figure 7 shows a plant treated with this combination treatment in comparison with one treated with calcium nitrate alone.

Hydrogen cyanamide plus sodium nitrate—*tomato*.—It was not known whether the accentuation of hydrogen cyanamide injury with calcium nitrate additions was due to the calcium or nitrate ion. To throw light on this problem a treatment involving the use of sodium nitrate plus 200 ppm hydrogen cyanamide (XVI) was used.

The details of the results of this treatment are not given since they are essentially the same as those obtained with the calcium nitrate and hydrogen cyanamide combination treatment.

These plants had a more sudden appearance of injury and a more severe type than did plants treated with 200 ppm hydrogen cyanamide alone. Since this was also true with calcium nitrate additions to the hydrogen cyanamide nutrient solutions, it is assumed that the nitrate ion accentuated the injurious effect of a relatively high concentration of hydrogen cyanamide. Schreiner and Skinner (43) have reported that guanidine injury was augmented by additions of nitrate nitrogen.

Hydrogen cyanamide in sand-colloid mixtures—*tomato*.—The purpose of this phase of Series 1 was to determine the possibility of growing the tomato in a mixture of sand and some suitable catalyst when hydrogen cyanamide was supplied as a source of nitrogen. Such a system with a constant drip of solutions would seem to offer some possibilities for investigating the utilization of the nitrogen from hydrogen cyanamide by plants.

Fig. 7.—Plant 28 (left). Calcium nitrate in the nutrient solution.
Plant 31 (right). Calcium nitrate plus 200 ppm hydrogen cyanamide in the nutrient solution. (Picture taken 37 days after the start of the experiment).
Inset. Injured tomato roots from plant receiving calcium nitrate plus 200 ppm hydrogen cyanamide in the nutrient solution. (Picture taken 3 days after start of the treatments).

Prehnite, a zeolitic mineral with the formula ($H_2Ca_2Al_2(SiO_4)_3$), was found by Crowther and Richardson (13) to be a suitable catalyst. Rhodin (39) found that animal charcoal was an efficient catalyst of the hydrogen cyanamide to urea change. In addition to these materials, kaolin, various types of bentonite clay, pulverized filter paper, and certain gels were used in this study.

Prehnite was ground as fine as possible and mixed with silica sand in a ratio of 10 per cent prehnite and 90 per cent sand by volume. In another set of pots the sand was mixed with animal charcoal powder in a ratio of 5 per cent charcoal and 95 per cent sand.

After the plants growing in these media developed minus nitrogen symptoms, treatments with 100 ppm hydrogen cyanamide in the nutrient solution (VI) were initiated.

On the twelfth day it was apparent that both sets of plants were growing with hydrogen cyanamide as an indirect source of nitrogen. Urea was found microchemically in the roots of plants growing in both of these mixtures. A trace of ammonium was found in the roots also. The urea formed in the hydrolysis of the hydrogen cyanamide was apparently a satisfactory source of nitrogen for the plants.

After the twelfth day, daily additions of several milliliters of urease extract prepared according to Morrow (32) were made to each 2 quarts of nutrient solution. The purpose of this addition was further to hydrolyze the urea to ammonia.

By the twenty-fifth day it was obvious that the plants in these mixtures were growing very satisfactorily with hydrogen cyanamide acting as the indirect source of nitrogen. It should be noted that the pH of the nutrient solution as supplied was 4.6; this reaction is too low for optimum utilization of ammonium nitrogen. Such a low reaction for the nutrient solution was necessary to prevent polymerization of the hydrogen cyanamide to dicyandiamide.

To demonstrate the complete picture of the growing of plants in such an artificial medium with hydrogen cyanamide as an indirect source of nitrogen, an attempt was made to nitrify the ammonium nitrogen in the cultures to nitrates. Several additions of nitrifying bacterial extract were made but nitrification was a failure. Nitrates could not be detected in either the roots or in the drainage solution from the pots. The constant drip of solutions may have washed the bacterial cultures out of the pots or the reaction of the medium may have been too acid for activity of the bacteria.

As indicated by the growth of the plants, the charcoal-sand mixtures produced better catalysis of the change to urea than did the prehnite-sand mixtures. Figure 8 shows a plant grown in pure sand and receiving 100 ppm hydrogen cyanamide in the nutrient solution as compared to one grown in a sand-charcoal mixture with the same concentration of hydrogen cyanamide.

A sample of the whole stems was taken from plants treated with hydrogen cyanamide plus urease in these sand-colloid mixtures for ammonium nitrogen determinations. On a dry-weight basis there was 0.398 per cent of ammonium nitrogen in the stems. This is a figure which is very comparable to that obtained by Tiedjens and Robbins (47) on tomato stems from plants supplied with ammonium nitrogen at a reaction of pH 4.0. In other words, the reaction of the growing medium was too acid for optimum ammonium utilization and a rather large amount accumulated in the stems.

In addition to the sand-colloid mixtures already mentioned, certain other colloidal agents were employed in an attempt to discover some cheap hydrolyzing agent to mix with the sand. Preliminary tests indicated that ground filter paper, ground paper pulp, aluminum hydroxide, silica gel, agar-agar, and kaolin were unsatisfactory agents.

Various types of bentonite clay were used as colloidal agents for this purpose. Bentonite clay of the "Volclay" brand was treated with hot calcium chloride to produce a calcium bentonite. Another sample of the clay was treated with dilute sulfuric acid to produce a hypothetical hydrogen clay. The reaction of the untreated bentonite was pH 7.80, that of the calcium bentonite was 6.10, and that of the hydrogen bentonite was 1.00. These three types of clay were mixed with white silica sand in the proportion of 3 per cent clay and 97 per cent sand by volume. The mixtures were placed in pots and flushed with water to free them of excess acid or chlorides. Nitrogen-starved tomato plants were placed in these pots and hydrogen cyanamide (Solution VI) was used as a source of nitrogen. Approximately 10 milliliters of urease extract were added to each 17 liters of nutrient solution.

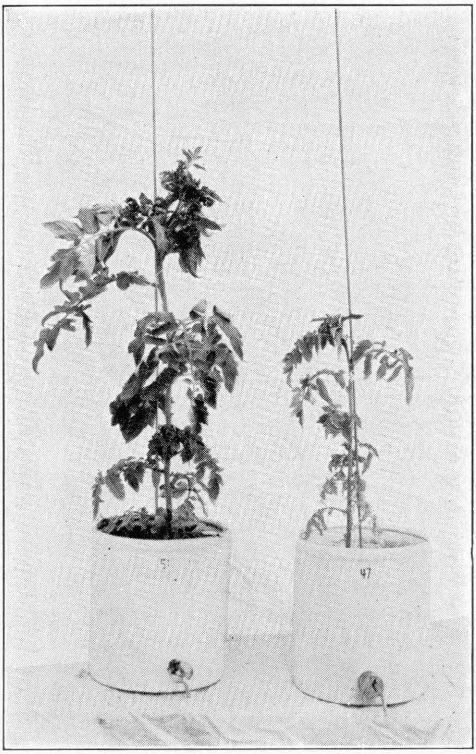


Fig. 8.—Plant 51 (left). 100 ppm hydrogen cyanamide in the nutrient solution. Plant growing in sand-charcoal mixture.

Plant 47 (right). 100 ppm hydrogen cyanamide in the nutrient solution. Plant growing in pure sand. (Picture taken 37 days after start of the treatments).

The plants in the calcium bentonite - sand mixtures grew almost as well as those in the sand-charcoal mixtures. Those grown in the acid and untreated bentonite-sand mixtures were green but grew very little during the period of the treatment.

Urea—*peaches.*—A review of the literature relative to the utilization of urea by plants is not pertinent to this discussion, but it may be said that the bulk of the evidence indicates that urea may be absorbed *per se* by many plants and serve as a source of nitrogen. A feature of this study was to determine what its effects on the peach and tomato were in comparison to certain other Cyanamid decomposition products.

Urea was supplied to one-year-old peach seedling trees at a concentration of 100 ppm (II) after initial signs of nitrogen deficiency were apparent in the foliage.

By the twenty-third day the trees were growing very well and had dark green foliage, although not quite as dark as that on trees supplied with sulfate of ammonia. It should be noted, however, that the urea-treated trees were not receiving as much total nitrogen as were those treated with sulfate of ammonia. The urea-treated trees seemed to have more fine, fibrous roots than did those supplied with other available nitrogen sources.

Urea—*tomatoes.*—Tomato plants were supplied with 100 ppm urea in the nutrient solution (II).

By the twenty-third day the urea-treated plants had made a very vigorous growth and the foliage was a dark green.

Ammonium sulfate—*peaches and tomatoes.*—A very extensive literature has accumulated regarding the utilization of ammonium nitrogen by plants. Only particularly relevant citations will be given in the following discussion. Tiedjens and Robbins (47) and Tiedjens and Blake (48) have found that ammonium nitrogen *per se* is absorbed by certain horticultural plants and may be assimilated, providing the reaction of the growing medium is not limiting.

Ammonium nitrogen is one of the final decomposition products of Cyanamid, and an inclusion of its performance in this investigation seemed desirable for comparative purposes.

Sulfate of ammonia in the nutrient solution (I) was supplied to both peach seedling trees and tomatoes at a reaction of pH 6.5.

Very vigorous peach trees and tomato plants were obtained with this type of treatment. The foliage was dark green and the roots were very extensive.

Calcium nitrate—*tomato.*—Nitrates are the final decomposition product of calcium cyanamide in the soil under moderately acid conditions. Although it is well known that nitrates can be efficiently utilized by plants when internal and external conditions are not limiting, both calcium and sodium nitrate were included in this study for comparative purposes.

Calcium nitrate at a concentration of 1380 ppm in the nutrient solution (III) was supplied to tomato plants. Plants receiving this treatment were very large and the leaves were extremely large and dark green in color. Figure 7 shows a plant which has received this treatment.

Sodium nitrate—*peaches, apples, and tomatoes.*—Peach and apple trees and tomato plants were supplied with 798 ppm sodium nitrate in the nutrient solution (XV). The reaction of the nutrient solution was pH 4.85.

Very vigorous, large trees and tomato plants were obtained with this type of treatment.

Guanidine—*tomato.*—Guanidine is not one of the principal decomposition products of Cyanamid but it may be present in the soil in small amounts following Cyanamid applications. Schreiner and Skinner (43) found that guanidine was harmful to potatoes, corn, and wheat. The injury was described as a "spotted condition in the foliage and stems followed by collapse of the plants". Asparagine seemed to counteract the ill effects of guanidine.

Guanidine was supplied, as the sulfate, to the tomato at a concentration of 100 ppm in the nutrient solution (XIII). A single plant was treated in this instance.

The treatment was continued for 37 days; the plant made no growth during this period. A leaf tipburn became apparent and the stems and petioles were hard and woody. There was no visible injury to the roots. With the exception of the injured leaf tips the plant was very comparable to one suffering from extreme nitrogen deficiency (Fig. 9).

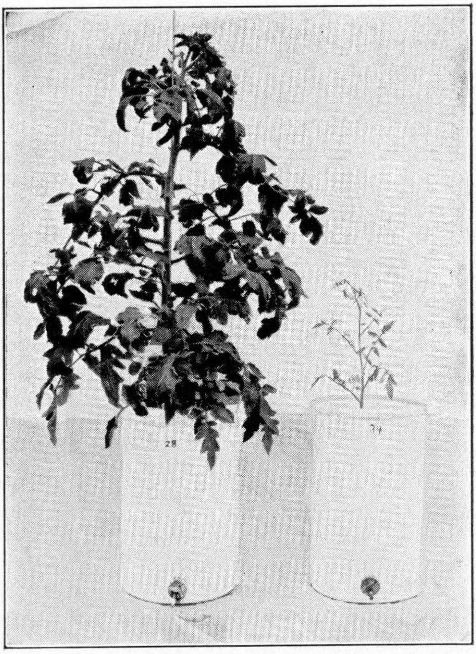


Fig. 9.—Plant 28 (left). Calcium nitrate in the nutrient solution.
Plant 34 (right). 100 ppm guanidine sulfate in the nutrient solution. (Picture taken 37 days after the start of the treatments).

Dicyandiamide—*peaches*.—A review of the literature revealed that dicyandiamide was injurious to a number of plants in rather small concentrations. The exact concentrations necessary to produce injury and the specific effects on the plants have been studied in soils, but little effort has been directed towards its effects when supplied in sand cultures.

Aso (3) suggested that amounts exceeding 0.01 per cent of the nitrogen from dicyandiamide would result in a typical leaf "burn". Inouye (22) found that amounts of dicyandiamide in which 80 pounds or less per acre of nitrogen were supplied were not harmful to rape or barley. Perotti (36) stated that amounts of dicyandiamide exceeding one per cent were injurious to wheat and corn in soil cultures.

The purpose of this phase of the experiment was to determine the concentration of this compound that would cause injury to the peach, apple, and tomato growing in sand cultures and to observe some of its effects. Preliminary work done with Grimes Golden apple trees had indicated that approximately 50 ppm were injurious to the apple.

One-year-old peach seedling trees were supplied with 25, 50, and 100 ppm of dicyandiamide in nutrient solutions IX, X, and XI, respectively.

By the twelfth day after the start of the treatments, all of the trees were showing some injury. The injury was barely discernible at a concentration of 25 ppm but was rather severe at 100 ppm. The first indication of injury was the appearance of brown tips on the leaves. Later the whole margins of the leaves became involved and soon were brown and dead.

By the fourteenth day the leaves on the trees receiving 100 ppm started to fall off. Injury was becoming progressively worse on the other treatments also.

By the seventeenth day the trees receiving 50 ppm started to lose their leaves and by the twenty-third day those receiving 25 ppm showed the same effect. On this last date the trees treated with 100 ppm had lost approximately one-half of their leaves. The leaves remaining on the trees treated with this compound at all concentrations had a more translucent yellow cast than did those receiving no nitrogen at all.

Treatments were discontinued on the twenty-fifth day. All of the trees had a typical minus nitrogen appearance. There was no marked injury to the roots but a few of them had injured tips. Every leaf that did not fall had the typical marginal injury all the way around the leaf. Figure 10 (Bottom) shows a tree receiving dicyandiamide in the nutrient solution as compared with one that had been treated with a very large Cyanamid application in soil.

A 14.5-gram sample of peach leaves from trees receiving 100 ppm of dicyandiamide was analyzed for dicyandiamide. The test was positive, there being a considerable formation of the crystalline precipitate. A 49.0-gram sample of the roots from these trees also had a positive test for dicyandiamide.

Dicyandiamide—*apples*.—One-year-old apple seedling trees were treated with 50 ppm dicyandiamide in the nutrient solution (X). These trees were not typical of minus nitrogen trees at the initiation of these treatments but the 27-day period of nitrogen starvation was deemed to be long enough for the purposes of the test.

On the eleventh day after the start of the treatments, a few of the leaves in the lower portions of the trees had black tips. There was a very slight fading of the chlorophyll around the margins of the leaves and in scattered spots throughout the leaves. There was no visible injury to the roots at this date.

Injury became progressively worse as the treatments continued, and by the twenty-seventh day there were prominent white spots throughout the leaves in a stippled fashion and the margins of many of the leaves were brown and dead.

Treatments were discontinued on the thirty-seventh day. The margins of almost all of the leaves were brown and dead; the lower leaves were particularly affected. Only a few roots had slightly injured tips. There were prominent white stipples throughout the leaves (Fig. 10 Top).

A 75-gram sample of the leaves taken for dicyandiamide analysis gave a negative result. A 22-gram sample of the roots also gave a negative test for dicyandiamide.

Dicyandiamide—*tomato*.—Concentrations of 25 and 50 ppm of dicyandiamide in nutrient solutions IX and X, respectively, were used with the tomato.

By the eleventh day after the start of the treatments the leaves on plants supplied with these concentrations had white or faded leaf margins. Many of the leaves had brown tips as well as white margins. Injury started at the leaf tips and soon the whole margins were involved. Injury at this date was worse at the higher concentration.

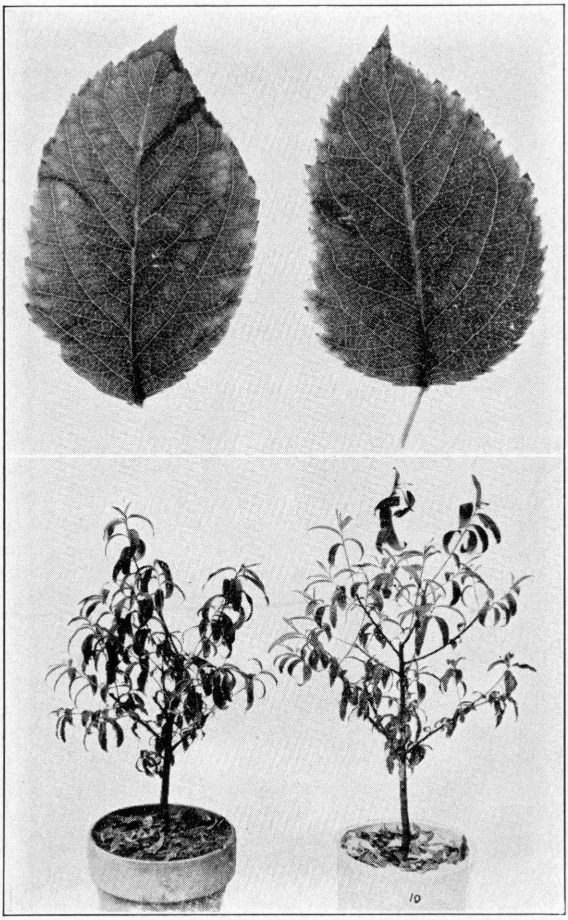


Fig. 10.—*Top*—Apple leaves from tree treated with 50 ppm of dicyandiamide in the nutrient solution. (Picture taken 28 days after the start of the treatments).

***Bottom*—Peach tree in soil on left injured by large Cyanamid application.**
Tree in sand on right treated with 100 ppm dicyandiamide in the nutrient solution.

Treatments were discontinued on the twenty-third day. Plants supplied with 25 ppm were very small and stunted and had made no more growth than plants supplied with minus nitrogen solution. The margins of the leaves were white or brown. The tips of all leaves were brown and dead. The plants had a typical nitrogen-deficient appearance; but there was no apparent injury to the roots. The plants treated with 50 ppm had a more severe type of injury but of the same general nature. A few root tips were brown and dehydrated at both concentrations.

Dicyandiamide plus sodium nitrate—*tomato.*—It has been shown that dicyandiamide was injurious in sand cultures in rather low concentrations. This material has been shown to be an unavailable source of nitrogen to these horticultural plants in sand cultures. The problem remained as to what the effect of this compound would be if an available nitrogen compound were added to the nutrient solution.

Nitrogen-starved tomato plants were treated with a solution (XVII) containing 50 ppm dicyandiamide in addition to 798 ppm sodium nitrate.

Within 3 days after the start of the treatments the plants had made visible recovery from nitrogen starvation. On the seventh day there was a slight tip burning on the foliage of the plants. The margins of a few leaves were faded. The plants were growing just as well as plants receiving sodium nitrate nutrient solution without the dicyandiamide. On the eighteenth day these plants had as much total growth as did plants receiving sodium nitrate nutrient solution. Almost every leaf had a white margin and a brown tip, however. A few slightly injured root tips were observed. The treatments were discontinued on the twenty-second day.

A 4.62-gram sample of leaves from a plant treated with dicyandiamide in addition to sodium nitrate was tested qualitatively for dicyandiamide. The test was negative.

Guanylurea—*peach.*—Allison *et al.* (1) found that guanylurea as the sulfate was a poor source of nitrogen to plants growing in soil and that in many cases it seemed to be inert and to retard growth.

Uniform one-year-old peach seedling trees supplied with a nutrient solution (XII) containing 100 ppm of guanylurea sulfate were studied for 25 days.

By the twenty-second day the trees supplied with this compound were markedly deficient in nitrogen. Their condition was comparable to that of trees supplied with a minus-nitrogen nutrient solution. During the treatment period the trees made no growth, although there was no visible injury to either roots or foliage.

Guanlyurea—*tomato.*—Guanylurea as the sulfate was supplied to the tomato at a concentration of 100 ppm in the nutrient solution XII.

Treatments were discontinued after 25 days. The plants so treated were typical of nitrogen-deficient plants. There was no injury to either roots or foliage.

Minus nitrogen—*peach, apple, and tomato.*—For purposes of comparison peach and apple trees and tomato plants were supplied with a solution (XIV) lacking in any nitrogen compound. Extreme nitrogen-deficiency symptoms were visible before the treatments were stopped.

EXPERIMENT II: SERIES 2

This series consisted of a group of miscellaneous studies with Cyanamid and certain of its decomposition products. One of the purposes of this series was to examine the gross effects of injurious concentrations. This study was confined to the visible and gross results of such injurious concentrations.

Hydrogen cyanamide injury.—Small tomato plants were grown in water cultures with concentrations of hydrogen cyanamide ranging from 25 to 200 ppm, at 25 ppm intervals. In this type of growing medium injury seemed to be caused by concentrations above 100 ppm. Microscopical examination revealed that the injured roots were plasmolyzed and the gelatinous covering of the roots was very thick and viscous.

The effects of various hydrogen cyanamide concentrations were also studied with certain species of algae. It had been noted in the greenhouse that a certain alga would grow in the nutrient solutions containing hydrogen cyanamide if the concentration did not exceed 150 ppm.

This alga, *Chlorococcum humicolum*, was supplied with various concentrations of hydrogen cyanamide in watch glasses and observed periodically with the microscope. The bodies of this alga were so small and opaque that the full details of even the gross effects could not be noted. It was observed, however, that there was a harmful effect within 48 hours from 150 ppm of hydrogen cyanamide, but not in 24 hours. Injury was characterized by a fading of the chlorophyll in the plastids and by somewhat of a plasmolysis of the plastids.

Sterile Spirogyra were also treated with different concentrations of hydrogen cyanamide. It was found, however, that this alga was affected by a solution of potassium phosphate which had an osmotic concentration equal to that of a harmful concentration of hydrogen cyanamide. The effect of 200 ppm hydrogen cyanamide was much more sudden than that of an equal concentration (i. e., osmotic) of potassium phosphate. The plastids were completely plasmolyzed by this treatment.

A supplement to this study was made with wheat plants grown in water cultures. With a treatment of 200 ppm hydrogen cyanamide there was a noticeable plasmolysis of the protoplasm of the root hairs in 2 hours.

Cyanide injury.—There is much loose usage of the term "cyanide injury" in the literature discussing Cyanamid investigations. Theoretically, it is impossible for any cyanide gas to be formed from Cyanamid in the normal decomposition process. According to Conant (9) it requires heating with a suitable catalyst to a temperature of 300° C. to produce any cyanide from Cyanamid. The purpose of this experiment was to indicate the effects of cyanide gas when supplied to the roots of tomato plants in sand cultures.

Tomato plants were grown in sand cultures and the tops of the pots were sealed over with sealing wax. A solution of 25 ppm potassium cyanide was allowed to drip upon the sand in one case, and in another 50 ppm of potassium cyanide were in the nutrient solution. The cyanide solutions flowed through the seals by means of a tube and then were permitted to drop upon the sand beneath the seals. The solutions volatilized when they reached the sand and there was a strong odor of cyanide gas. Treatments were continued for 9 days with these concentrations.

After 9 days the concentrations were increased to 100 and 200 ppm since the former concentrations were not sufficient to produce more than a slight injury, and this occurred only with the 50 ppm concentration. After 4 days of treatment with the increased concentrations the roots of these plants appeared very badly injured. There were no noticeable effects on the foliage other than wilting on hot days. These plants were analyzed for free and combined cyanide but none could be detected.

The use of large Cyanamid applications.—The purpose of this test was to determine how much Cyanamid is required to injure peach and apple trees grown under orchard conditions in a Wooster silt loam soil.

The Cyanamid was in no case mixed with the soil, being merely broadcast over the surface under the spread of the branches. The peaches were in a cultivated orchard and the apples in a sod orchard.

On April 20, 1932, 2 pounds of granular Cyanamid were applied to two 9-year-old peach trees in the Ohio Experiment Station Variety Orchard which improved the color of the foliage and caused no injury.

On June 30, 1932, 2 and 3 pounds, respectively, of granular Cyanamid were applied to two 9-year-old peach trees. There was no resultant injury and the trees had a very dark green foliage thereafter. On September 9, 1932, 2 pounds of material were given to the same tree that had the 2-pound treatment on June 30 and 3 pounds were given to the tree that had been given 3 pounds on June 30. Again no injury resulted.

On June 16, 1933, a 15-year-old apple tree was given 10 pounds of granular Cyanamid. It rained on June 16 and then not again for over a week. There was no apparent injury to the tree but the grass was badly burned. In August of 1933 this same tree was again treated with 15 pounds of material but still no injury resulted.

On June 16, 1933, a 10-year-old peach tree was given 8 pounds of material in the fertilizer ring and then again in August of that year it was treated with 10 pounds. No injury resulted.

The foregoing observations do not mean that Cyanamid can always be applied without regard to the rate or season of the year without fear of injuring the trees since cases of injury are reported. On very sandy or alkaline soils these amounts would probably have caused injury.

DISCUSSION OF EXPERIMENT II

Hydrogen cyanamide.—Concentrations of hydrogen cyanamide as low as 50 ppm proved injurious to the tomato and higher concentrations were even more harmful.

Moreover, additions of either sodium or calcium nitrate to the hydrogen cyanamide nutrient solutions caused an accentuation of injury. Not only were these plants more severely injured than plants receiving hydrogen cyanamide alone but they made very little growth even though there was an adequate supply of available nitrogen.

Likewise, a concentration of 200 ppm of hydrogen cyanamide proved very injurious to the peach and the apple.

Hydrogen cyanamide injury is accentuated by hot weather. It is thought that this influence is due to the fact that the roots are seriously affected by hydrogen cyanamide treatments.

In no case was hydrogen cyanamide detected qualitatively inside of plants treated with this compound. Either the effect of this compound is extremely local (i. e., on the roots) or else the test employed does not detect small concentrations of the compound in the plant. The latter explanation is a very likely possibility.

The effect of injurious concentrations of this compound on plant cells seems to be a rather typical plasmolysis of the protoplasm.

When suitable catalysts were added to sand, hydrogen cyanamide was hydrolyzed to urea, and concentrations as high as 150 ppm of hydrogen cyanamide were not injurious to tomato plants. Plants grew very satisfactorily in sand-colloid mixtures to which hydrogen cyanamide was added as an indirect source of nitrogen. Additions of urease to the nutrient solution hydrolyzed the urea to ammonia and the plants utilized the ammonium nitrogen.

Silica gel, agar-agar, pulverized filter paper, ground paper pulp, aluminum hydroxide, kaolin, sodium bentonite clay, and hydrogen bentonite clay proved to be unsatisfactory catalysts in these sand-colloid mixtures. Confirmation of the work of other investigators who found prehnite and animal charcoal effective catalysts is offered. Calcium bentonite clay was found in this study to be an effective catalyst of the hydrogen cyanamide to urea change also. It is not quite as good as animal charcoal, however. No explanation of the nature of the catalysis is offered.

Dicyandiamide.—In sand cultures a concentration of 25 ppm of dicyandiamide proved harmful to the tomato. The availability of the nitrogen of this compound in pure sand is negligible.

In the presence of sodium nitrate, dicyandiamide was still injurious to the tomato. Although it produced no lessening of growth of the plants, the foliage was slightly burned.

Injury of the peach by dicyandiamide was indicated by rather regular brown, dead areas around the margins of the leaves. Defoliation followed the injury to the foliage. At higher concentrations some root tips were affected.

A concentration of 50 ppm of dicyandiamide injured apple seedling trees in sand cultures.

Guanidine and guanylurea.—Guanidine and guanylurea as the sulfate were both unsatisfactory sources of nitrogen in sand cultures. Each was supplied in the nutrient solution at a concentration of 100 ppm. The former was slightly harmful to the tomato at this concentration, but the latter was non-injurious to both the tomato and peach.

Usage of the term "cyanide" injury in describing effects of large and improperly made applications of Cyanamid is wholly unjustified.

EXPERIMENT III

The purpose of this experiment was to determine at what soil reaction Cyanamid nitrogen was most efficiently used by the peach and apple.

The Canfield silt loam soil used in this study was first placed in a greenhouse bench in 1929. It was modified in soil reaction at that time and used in soil reaction studies prior to this experiment. The pH of the soil was modified at 0.5 intervals from 4.5 to 8.0. It was found that the content of active aluminum was so high in the 4.5 plot that this reaction value was eliminated from the experiment.

At the time the soil was placed in the greenhouse bench a small amount of peat moss was incorporated with it and a small application of ammonium sulfate was made. After that time no nitrogen was added.

Peach seeds were planted in each soil reaction bed May 9, 1932, and apple seeds were planted December 5, 1931. The seeds were planted in single rows; after the trees were 6 to 24 inches high they were transplanted. Each soil reaction bed was divided into two sections (i. e., Plot 1 and Plot 2) and four peach trees and five apple trees were planted in each section. Each plot at each soil reaction value was 12.32 square feet.

The reaction of the soil was modified throughout the experiment by the use of aluminum sulfate or sulfur (the latter being used during the latter part of the study) and hydrated lime. The various amounts of reaction-modifying materials used were estimated from the data of Barnes (5). The materials were well mixed with the surface inch of soil.

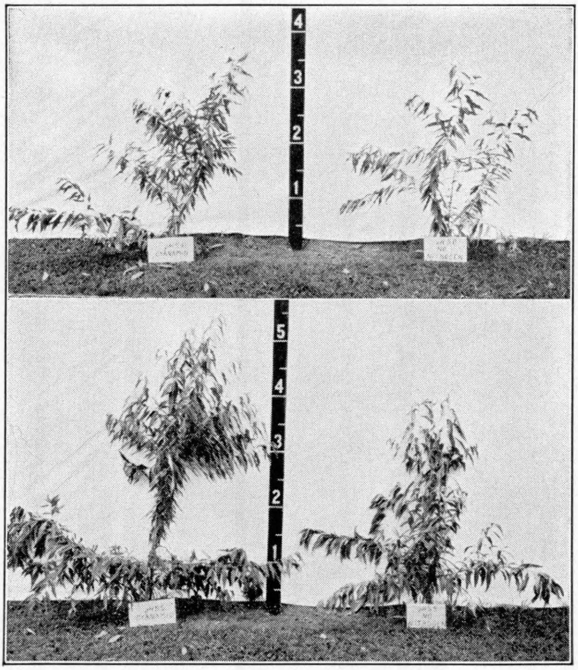


Fig. 11.—*Top*—Cyanamid-treated and untreated peach trees at a soil reaction value of pH 5.0. *Bottom*—Cyanamid-treated and untreated peach trees at a soil reaction value of 5.5 pH.

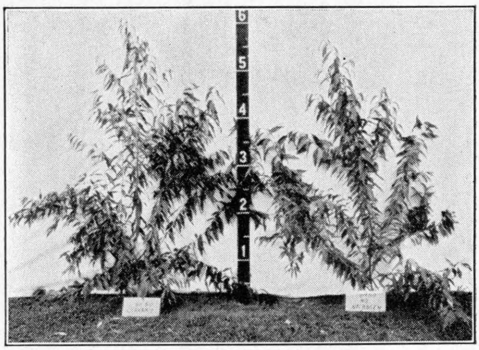


Fig. 12.—Cyanamid-treated and untreated peach trees at a soil reaction value of pH 6.0.

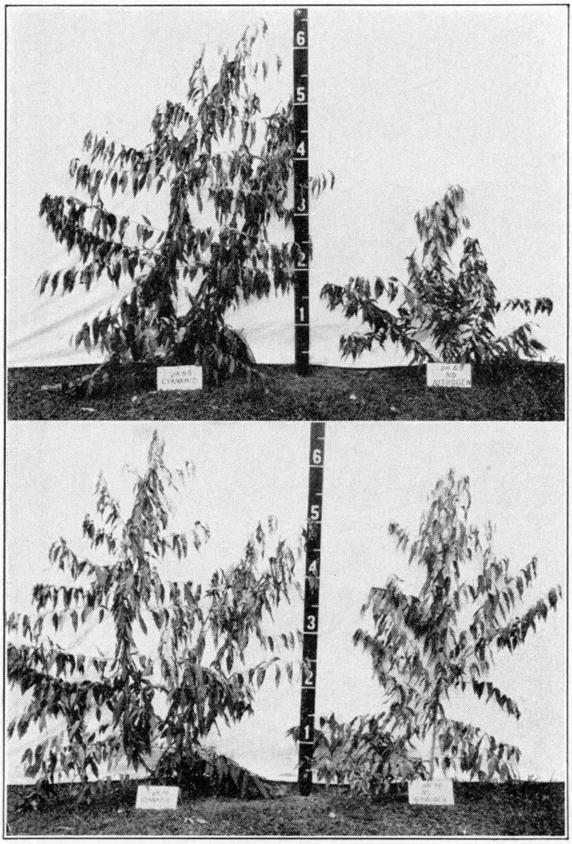


Fig. 13.—*Top*—Cyanamid-treated and untreated peach trees at a soil reaction value of pH 6.5.

Bottom—Cyanamid-treated and untreated peach trees at a soil reaction value of pH 7.0.

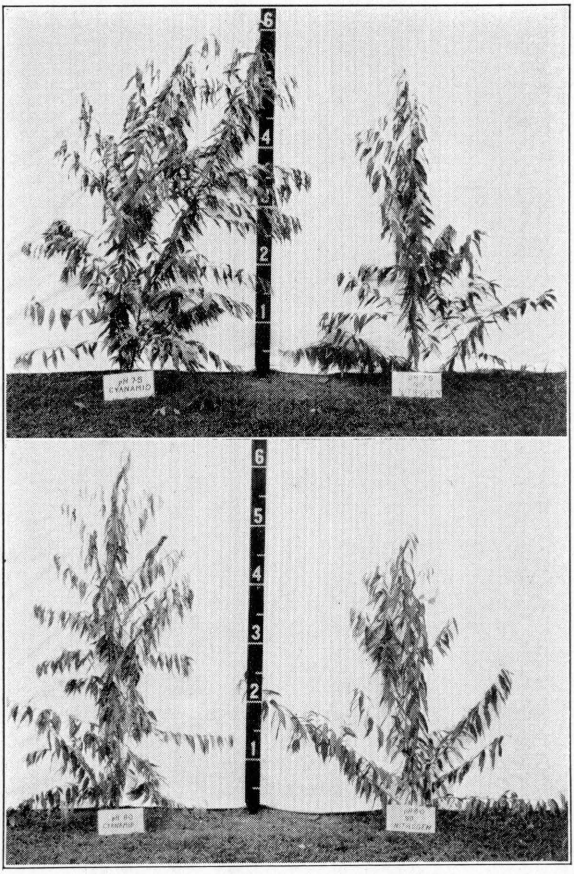


Fig. 14.—*Top*—**Cyanamid-treated and untreated peach trees at a soil reaction value of pH 7.5.**

Bottom—**Cyanamid-treated and untreated peach trees at a soil reaction value of 8.0.**

The soil reaction values which were periodically determined appear in Table 6. Difficulty was experienced with the soil reaction modification procedure due to the large number of roots in the surface of the soil after the study was well under way. Additions of Cyanamid to one plot at each reaction value also complicated matters somewhat, due to the alkalinizing effect of this material.

TABLE 6.—Soil Reaction Values in Greenhouse Bench Plots

Desired soil pH	6/21/32 pH	7/27/32 pH	8/8/32 pH	9/14/32 pH	12/27/32 pH	3/28/33 pH	4/25/33 pH	5/31/33 pH	6/18/33 pH	7/3/33 pH
Cyanamid-treated										
5.0	4.78	5.03	4.60	5.10	5.60	5.40	5.60	4.80	5.57	5.30
5.5	5.46	5.40	5.70	6.10	6.20	6.00	5.39	5.96	5.45	5.72
6.0	5.71	6.28	6.30	6.70	6.60	6.40	5.83	5.73	5.12	6.02
6.5	6.31	6.55	6.90	6.75	7.20	6.60	6.79	6.36	7.14	6.56
7.0	6.93	7.10	7.10	7.78	7.40	7.40	6.63	6.40	6.50	7.20
7.5	8.03	7.88	8.25	8.30	8.00	8.00	7.47	6.92	7.35	7.50
8.0	8.05	8.20	8.50	8.24	8.20	8.20	7.90	6.70	7.97	7.89
Untreated										
5.0	4.86	5.03	....	5.00	5.40	5.00	4.70	4.37	5.16	5.77
5.5	5.46	5.40	....	6.10	5.60	5.80	5.27	5.98	5.27	5.80
6.0	6.05	6.28	....	6.40	6.40	6.00	5.67	5.30	6.25	6.50
6.5	6.48	6.55	....	6.90	6.80	6.00	5.76	5.90	6.65	6.40
7.0	6.56	7.10	....	6.90	7.20	7.40	7.38	6.20	7.20	6.90
7.5	7.56	7.88	....	7.78	7.80	8.00	7.75	7.65	7.48	7.40
8.0	7.35	8.20	....	8.20	8.20	8.20	7.98	7.60	8.20	8.10

Tap water was used for watering the trees as often as seemed desirable for the best growth of the trees.

Treatment of one plot at each soil reaction value was made on August 8, 1932, with pulverized Cyanamid at the rate of 400 pounds to the acre. One plot was left untreated. It was noted that the treated trees had a greener foliage than did the untreated trees before the trees entered the dormant period. The treated trees were also slower in entering the dormant period than were the untreated ones.

On December 27, 1932, a second treatment of one plot was made with granular Cyanamid at the rate of 400 pounds to the acre.

Very prolific growth was made during the 1933 season on both the untreated plots and the treated ones. For some unexplainable reason the peach trees in the untreated plot at pH 6.5 were all small.

The experiment was discontinued on July 18, 1933, and the trees were measured and weighed. Leaves and roots of the peach trees were taken for nitrogen analyses.

Results of the experiment as indicated by weights of the tree tops and the primary linear growth of shoots appear in Tables 7 and 8. The peach data indicate that the best growth of untreated trees was at pH 6.0. The greatest growth of Cyanamid-treated trees was at pH 7.5, and the greatest difference between treated and untreated trees was at pH 7.5.

The apple data indicate that the best growth on the untreated plot was at pH 7.0. The best growth on the treated soil was at pH 7.0, and the greatest difference between treated and untreated trees was at pH 7.0.

TABLE 7.—Average Weights of Tops of Trees at the End of 1933 Growing Season in Various Soil Reaction Plots

Soil pH	Apples		Peaches	
	Cyanamid	Untreated	Cyanamid	Untreated
	Gm.	*Gm.*	*Gm.*	*Gm.*
5.0	10.1	4.7	95.0	169.7
5.5	18.5	10.8	550.2	244.7
6.0	22.6	17.2	585.5	401.5
6.5	28.5	16.2	503.5	129.0
7.0	36.4	22.2	538.0	348.2
7.5	28.2	10.4	623.2	275.0
8.0	31.4	20.6	452.5	271.0

TABLE 8.—Average Primary Linear Branch Lengths at End of 1933 Growing Season in Various Soil Reaction Plots

Soil pH	Apples		Peaches	
	Cyanamid	Untreated	Cyanamid	Untreated
	In.	*In.*	*In.*	*In.*
5.0	14.6	8.0	105.0	162.5
5.5	17.3	18.2	382.2	205.2
6.0	20.2	19.0	331.5	342.2
6.5	33.7	17.7	310.7	133.3
7.0	38.3	20.5	305.7	229.2
7.5	28.0	23.4	414.0	284.7
8.0	31.3	27.2	383.0	230.5

Nitrogen determinations on the leaves of the peach trees appear in Table 9. The results indicate that with one exception there was more total nitrogen in peach leaves from Cyanamid-treated trees than in those from untreated ones. There seemed to be somewhat more total nitrogen at pH 5.0 in the leaves from Cyanamid-treated trees than at other reaction values. The trees at pH 5.0 were also considerably smaller than those at other reaction values. There was somewhat more total soluble nitrogen at pH 5.0 than at any other value in the Cyanamid-treated trees. Undoubtedly, organic nitrogen synthesis was more efficient at other reaction values than at 5.0. There was consistently more total soluble nitrogen in leaves from treated trees than in those from untreated ones.

TABLE 9.—Soluble and Total Nitrogen* in Leaves from Cyanamid-treated and Untreated Peach Trees at Various Soil Reaction Values

Soil pH	Cyanamid-treated		Untreated	
	Soluble N	Total N	Soluble N	Total N
	Pct.	*Pct.*	*Pct.*	*Pct.*
5.0	0.308	1.539	0.280	0.956
5.5	.205	1.100	.171	....
6.0	.239	1.038	.239	1.012
6.5	.239	.970	.215	.976
7.0	.260	.964	.137	.670
7.5	.286	1.085	.213	1.004
8.0	.280	....	.205	.831

*Results expressed as per cent of fresh weight.

Table 10 reveals that there was more total nitrogen in the roots of Cyanamid-treated peach trees than in those from untreated ones. There were no significant differences in the amounts of total nitrogen in the roots from trees at the different reaction values.

TABLE 10.—Total Nitrogen* in Cyanamid-treated and Untreated Peach Tree Roots at Various Soil Reaction Values

Soil pH	Cyanamid-treated	Untreated
	Pct.	*Pct.*
5.0	1.198	1.267
5.5	1.438	1.130
6.0	1.322	....
6.5	1.493	1.301
7.0	1.438	.957
7.5	1.325	1.061
8.0	1.233	1.096

*Results expressed as per cent of dry weight.

DISCUSSION OF EXPERIMENT III

Krotowiczowna (24) indicated that Cyanamid was efficiently used from pH 4.0 to 8.0 but that greatest response occurred on acid soils. Schmitt (42) found that good results were obtained with Cyanamid on acid soil with a number of crops.

In this investigation seedling apple trees treated with Cyanamid made the greatest growth at pH 7.0. The greatest growth of untreated trees was also at pH 7.0.

Cyanamid-treated peach seedlings made the greatest growth at pH 7.5. Untreated trees made the greatest growth at pH 6.0.

It would seem that both the peach and apple utilized the nitrogen from Cyanamid most efficiently at approximately the neutral point. Experiment I of this study showed that the nitrogen utilization of Cyanamid is in large part concerned with ammonium intake and assimilation. Tiedjens and Blake (48) have shown that the apple can best utilize ammonium nitrogen above the reaction of 6.5 pH. Hence, it is to be anticipated that Cyanamid nitrogen is best utilized by the apple and peach at approximately the neutral point.

It should be pointed out, however, that if such a large application of Cyanamid is made that the alkalinity produced permits dicyandiamide formation full utilization of the Cyanamid nitrogen is not possible.

PRACTICAL APPLICATIONS

Calcium cyanamide may be used over a rather wide range of soil reactions for the peach and apple with satisfactory results. However, best results may be expected at approximately the neutral point or below. The suggested explanation of this fact is that the utilization of calcium cyanamide nitrogen is essentially an ammonium nitrogen problem and this type of nitrogen is best utilized by the peach and apple in the less acid types of soil.

Continued use of calcium cyanamide lessens the acidity of the soil and thus creates a condition more suitable for the utilization of Cyanamid nitrogen than that found on very acid soils.

The usage of very large applications of calcium cyanamide with the peach and apple should be avoided, particularly on the lighter types of soil. If there are sufficient amounts of colloidal or clay material in the soil, Cyanamid may be applied in rather large amounts under orchard conditions providing the soil is not too alkaline. Wagner (50) pointed out that description of Cyanamid as a "toxic" fertilizer was unwarranted. Many fertilizing materials are "poisonous" when improperly used. Proper usage of Cyanamid should eliminate the possibilities of plant injury with this material.

A limited amount of data in this investigation indicated that better results may be expected on the heavier types of soil than on the lighter types with Cyanamid. Even though there is no plant injury with Cyanamid applications on the lighter types of soil, one may anticipate that results as indicated by plant growth may not be as good as those obtained on the heavier soil types. There is a more complete breakdown of the Cyanamid to ammonium and nitrates in the soil types containing plenty of clay material than in those deficient in it, and there is less leaching of the soluble decomposition products.

A study of different rates, methods, and times of application of Cyanamid to apple trees under orchard conditions is in progress in four orchards in widely scattered points in Ohio. This study has been under way for 3 years but has not yet reached the point where definite conclusions can be drawn from the tree growth and yield data. Tentative conclusions point to the fact that Cyanamid is a satisfactory fertilizing material for the apple on the soil types employed. A full report of this study will appear in a later publication.

SUMMARY

I. On the second to fifth day following Cyanamid treatments the ammonium content of the roots of both tomato plants and peach trees in soil cultures increased. Variations in the date of the increase seemed somewhat dependent upon the amount of colloidal or organic material in the growing medium. The greater the colloidal or organic content of the growing medium, the more quickly did an increase of ammonium appear in the roots. There was a persistence of this increase for 15 to 25 days following the date of the treatment.

II. Following the increase in the ammonium nitrogen content of the roots of the peach and tomato by one to several days, there was an increased amount of nitrates.

III. It is unlikely that urea serves as a direct source of nitrogen for plants in soil cultures following Cyanamid treatments.

IV. Macrochemical data indicate that Cyanamid-treated tomato plants had more ammonium, total soluble, and nitrate-ammonium free soluble nitrogen than untreated plants in two soil types. The utilization of Cyanamid nitrogen seems to be essentially an ammonium and nitrate phenomenon.

V. The effects of various concentrations of hydrogen cyanamide, dicyandiamide, guanidine, and guanylurea on the peach, apple, and tomato were studied. Details of the symptoms of injury of these compounds are given in the text. Injury by hydrogen cyanamide to the tomato is accentuated by the addition of nitrates to the nutrient solution. The presence of nitrate nitrogen does not seem to augment dicyandiamide injury with the tomato.

The effects of hydrogen cyanamide and dicyandiamide on the peach, apple, and tomato differ in both root and foliage characteristics.

Hydrogen cyanamide is a potential source of injury to the peach, apple, and tomato with Cyanamid applications on soils devoid of colloidal or organic matter.

Dicyandiamide is a potential source of injury with Cyanamid applications when extremely large and improperly made treatments are made or on highly alkaline soils.

VI. Tomato plants have been grown successfully in sand-colloid mixtures with constant drip of solutions using hydrogen cyanamide as an indirect source of nitrogen. Calcium bentonite was found to be an effective catalyst of the hydrogen cyanamide to urea change in sand-colloid mixtures, but it was slightly inferior to animal charcoal in this capacity.

VII. Guanidine and guanylurea are unlikely sources of difficulty when Cyanamid is applied to the soil.

VIII. Peach and apple seedlings grown in soil had the greatest weight of tops at pH 6.0 and 7.0, respectively. Cyanamid-treated peach trees made the greatest growth at pH 7.5, and Cyanamid-treated apple trees, at pH 7.0.

IX. Three years' results in the orchard indicate that Cyanamid is a satisfactory source of nitrogen for the apple when it is properly used.

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